PB86-163060

Proceedings: National Symposium on Recent Advances in Pollutant Monitoring of Ambient Air and Stationary Sources (5th Annual) Held at Raleigh, North Carolina on May 14-16, 1985

(U.S.) Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Jan 86

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Environmental Monitoring Systems
Laboratory
Research Triangle Park NC 27711

EPA/600/9-85/029
Jan. 1986

Research and Development

EPA

Proceedings:

PB86-163060

Fifth Annual National Symposium on Recent Advances in Pollutant Monitoring of Ambient Air and Stationary Sources

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA/600/9-85/029

2.

3. RECIPIENT'S ACCESSION NO.
PB86 1630607AS

4. TITLE AND SUBTITLE
PROCEEDINGS: Fifth Annual National Symposium on Recent Advances in Pollutant Monitoring of Ambient Air and Stationary Sources

5. REPORT DATE
January 1986

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
U. S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Monitoring Systems Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA/600/08

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The fifth annual national symposium sponsored by EPA's Environmental Monitoring Systems Laboratory was held May 14-16, 1985 in Raleigh, North Carolina. In seven sessions over three days, papers and discussions focused on state-of-the-art systems for monitoring source emissions, ambient air, acid deposition, method 25 and personal monitoring. This symposium is part of a continuing effort to explore recent advances in pollutant monitoring of ambient air and stationary sources. This publication is intended to assist those researchers concerned with furthering the science of air monitoring.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
281

22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA/600/9-85/029

Proceedings: Fifth Annual National Symposium on Recent Advances in Pollutant Monitoring of Ambient Air and Stationary Sources

Radison Plaza Raleigh Hotel
Raleigh, NC
May 14-16, 1985

Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Office of Research and Development
Research Triangle Park, NC 27711

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has the responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise and Radiation, the Office of Pesticides and Toxic Substances and the Office of Solid Waste and Emergency Response.

Thomas R. Hauser, Ph.D.
Director
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina

TABLE OF CONTENTS

INTRODUCTION 1

Session I - Acid Deposition

Application of Similarity Methods to Deduce Dry Deposition Covariances Using Imperfectly Responding Sensors 2

An Eddy Accumulator for Dry Deposition Measurements 7

A Prototype Concentration Accumulation Apparatus for Determining Time - Averaged Dry Deposition of Gaseous Pollutants 16

Simple Meteorological and Chemical Filterpack Monitoring System for Estimating Dry Deposition of Gaseous Pollutants 23

Evaluation of an Automated Tungstic Acid Technique for Nitric Acid and Ammonia 30

Application of the Tungsten Oxide Denuder Tube Technique to the Measurement of Nitric Acid in the Rural Troposphere and Comparison with the Nylon Filter Method 39

The Use of Lichens to Measure the Transport of Airborne Heavy Metal Pollutants 51

Measurement of HNO_3, SO_2, NH_3 and Particulate Nitrate with an Annular Denuder System 55

A New Analyzer for the Continuous and Unattended Measurement of Low Levels of Sulfur Dioxide in Ambient Air 72

Session II - General

Alkalinity Measurements in Evaluating Hi-Vol Filter Performance 79

A Procedure for the Isolation and Concentration of Milligram Quantities of Carbon Monoxide from Ambient Air 81

Analysis of the Effluents from Polyurethane Foam Insulation 88

Quantitative Analysis of PPB Concentrations of Hydrogen Sulfide in Air Using a Gold Film Sensor 92

Session III - Source Emission Monitoring Using EPA Reference Method 25

The State of Delaware Experience with EPA Reference Method 25 Audit Samples 99

Utilization of EPA Method 25 for the Measurement of Volatile Organic Carbon (VOC) Emissions from Combustion and Steam Sources 104

Preceding page blank

Session IV - Analysis of Chemical Complex Data

An Overview of the Development of Methods of Chemometric Methods 127

Cluster Analysis Applied to Individual Atmospheric Particles 130

Evaluation of Emission Data from Hazardous Waste Incineration Tests Using Pattern Recognition Techniques 134

Distributed Chemical Alarm Systems for Plant Security Based on Ion Mobility Spectrometry (IMS) 136

Session V - Personal Monitoring

Personal Monitoring: Overview 154

Indoor Aerosol Impactor 158

Analysis of Nitrite in NO_2 Diffusion Tubes Using Ion Chromatography 166

Evaluation of COED-1 Portable Carbon Monoxide Personal Exposure Monitors 171

Monitoring of Benzene in Ambient Air with Organic Vapor Badges 178

A Passive Dosimetry Method for Determining Hydrazine in Air 183

Session VI - Organic Pollutants

GC/FTIR Studies of Volatile Organic Compounds Collected on Tenax Cartridges 190

New Redox Reaction Processes for Analysis of Atmospheric Pollutants 204

Application of Multidimensional Gas Chromatography to the Analysis of Particulate Samples 209

A New Microprocessor-Based Instrument for Thermal Desorption of Adsorbent Traps 218

Comparison of Sample Collection Techniques for Volatile Organic Compounds in Ambient Air 226

Benzene and Toluene Concentrations in Lake Charles, Louisiana Ambient Air 237

Determination of 2-Diethylaminoethanol in Air 241

Analysis of Semi-volatile Organic Compounds Using Supercritical Fluid Methodologies 247

Session VII - Source Monitoring

Validation of an Emission Method for Inorganic Arsenic 253

Studies on the Dynamic Impinger Sampling System 258

Development of a Compact Total Reduced Sulfur (TRS) Continuous Emission Monitoring System 261

Measuring Volatilization Flux of Pesticides from Treated Surfaces 267

INTRODUCTION

The fifth Annual National Symposium on Recent Advances in the Measurement of Air Pollutants was held May 14-16, 1985 in Raleigh, North Carolina. The symposia are sponsored by the United States Environmental Protection Agency's (EPA's) Environmental Monitoring Systems Laboratory in Research Triangle Park, North Carolina.

This fifth annual symposium was part of a continuing effort to explore recent advances in pollutant monitoring of ambient air and stationary sources. It served as a forum for exchange of ideas and scientific information. In response to the Agency regulatory needs, this symposium focused on acid deposition, personal exposure and toxic substances. This publication is intended to assist those researchers interested in furthering the science of air monitoring.

Because several presenters listed in the Symposium announcement spoke extemporaneously and did not prepare a paper, the number of papers in these proceedings are fewer than the actual numbers of presentations.

APPLICATION OF SIMILARITY METHODS TO DEDUCE DRY DEPOSITION COVARIANCES USING IMPERFECTLY RESPONDING SENSORS

by

B. B. Hicks and R. T. McMillen
Atmospheric Turbulence and Diffusion Division
Air Resources Laboratory, ERL, NOAA
Post Office Box E, Oak Ridge, TN 37831

Introduction

Methods for measuring dry deposition rates are relatively few. Direct measurement of the accumulation of material at the surface is possible mainly for particulate species to surfaces like snow, or to surfaces that can be washed without damaging them (e.g. some foliage). Use of artificial surfaces or collection vessels is not widely favored because the collection characteristics of such devices are rarely similar to those of the natural surfaces they are meant to simulate. Most modern studies make use of micrometeorological methods, which, if properly applied, permit precise evaluation of fluxes through planes elevated above the surface. These measured fluxes are equal to surface fluxes if stringent site quality and temporal stationarity criteria are satisfied. However, an overwhelming difficulty is that such methods require sensors of precision and/or time resolution that are presently available only for very few chemical species.

Hicks (1979) addresses the matter of pollutant sensing requirements for micrometeorological applications. Several distinctly different factors arise to complicate the way in which micrometeorological methods can be applied to measure dry deposition rates. First, gradient methods require the use of sensors capable of resolving differences with 1% precision, if not better. Even if suitable chemical methods exist, the gradient method is accurate only over surfaces with relatively short vegetation.

Eddy correlation techniques do not require an assumption regarding eddy diffusivity, and hence tend to be preferred. However the requirement for fast response sensing limits the application to very few chemical species. In general, ± 10% accuracy evaluations of eddy fluxes require 1-second response time in daytime conditions, and sometimes as short as 0.1 second at night. Most transfer usually takes place in daytime.

The similarity principles addressed here permit fluxes of some trace species to be inferred from knowledge of another if appropriate gradient or turbulence intensity data are available to serve as a linkage. The constraint imposed by the surface heat energy balance involving (primarily) net radiation, sensible heat, latent heat of evaporation, and heat storage provides an opportunity to bypass the need for a direct flux measurement using micrometeorology. The method of present interest uses net radiation as a basis for calculations, and employs similarity principles first to derive the sensible heat flux and then to infer a dry deposition flux from knowledge of pollutant turbulence characteristics. In practice, net radiation is easily measured, using straight-forward sensors available from commercial sources.

Theoretical Considerations.

The so-called "similarity/heat-budget" method is based on apportionment of net radiation R_n between sensible and latent heats, and on the measurement of turbulence intensities of temperature and pollution concentration using sensors with matched frequency response.

The surface heat energy budget can be written as

$$H + LE = R_n - S \tag{1}$$

where H is the sensible heat flux, LE is the latent heat flux, and S is the rate of heat storage beneath the level of measurement. The Bowen ratio, β, is defined as H/LE, so that

$$H(1 + 1/\beta) = R_n - S \tag{2}$$

Now, suppose that a measure of pollutant concentration standard deviation σ_c is measured in some selected frequency band, and that similarly constrained (i.e. defined by the same frequencies) measures of temperature and humidity standard deviations are also obtained: σ_T and σ_q respectively. If the flux of pollutant is F, then similarity principles dictate that

$$F/H = \sigma_c/c_p\sigma_T \tag{3}$$

and

$$H/LE = \beta = c_p\sigma_T/L\sigma_q. \tag{4}$$

From here, trivial mathematical manipulation yields that

$$F = \sigma_c(R_n - S)/(c_p\sigma_T + L\sigma_q). \tag{5}$$

Equation (5) provides a means for evaluating a flux F from imperfect (but matched) standard deviation data σ_c, σ_T and σ_q, using measurements of net radiation as a basis. Over many agricultural surfaces, the heat storage term S is less than 15% of R_n, and in most circumstances can be taken to be about 10% of R_n, hence

$$v_d \cong 0.9(\sigma_c/C)\cdot R_n/(c_p\sigma_T + L\sigma_q), \tag{6}$$

where the deposition velocity v_d is defined as $F/\bar{C}$.

A somewhat simpler form of (6) might be of special interest in circumstances in which the Bowen ratio β can be computed from external information, such as by use of a combination formula derived from agricultural or agrometeorological considerations. In this case, the need for specific humidity data to yield σ_q can be avoided, since (6) can be rewritten as

$$v_d \cong 0.9(R_n/\bar{C})\cdot(\sigma_c/c_p\sigma_T)/(1 + 1/\beta). \tag{7}$$

From inspection of Equation (7), it is evident that the various sources of error combine such that the relevant proportional errors can be compounded as in

$$E(v_d)/v_d = E(\sigma_c)/\sigma_c + (1+\beta)^{-1}E(\beta)/\beta, \tag{8}$$

where E(x) is the error on x. The Bowen ratio β is normally positive in daytime, but typically less than unity over vegetation. Over sparse vegetation, or over bare soil, β can attain large positive values, such that the final term in (8) would then be insignificant. In general, however, the final term of (8) cannot be disregarded. Major interest focuses, however, on the term $E(\sigma_c)/\sigma_c$, since this is the factor which influences instrument design and application.

Inspection of Equation (7) indicates that deposition velocities can be estimated using sensors with deficient response provided quantities such as σ_c and β can be measured. Table 1 presents an example of results obtained in a field test conducted at the Walker

Branch Watershed field site during May, 1983. The data were obtained during a multilaboratory "core" research experiment conducted in collaboration with Argonne National Laboratory and Pennsylvania State University. The tabulation includes information on temperature, humidity, atmospheric sulfur concentration, and particle by smoothing records obtained with fast-response sensors to produce 1, 3, 10, and 30-second averages prior to computation. The results of Table 1 are typical of daytime, convective conditions. The nocturnal case has yet to be addressed in as much detail.

Figure 1 illustrates the consequences of high-frequency noise on the general utility of standard deviations as a basis for calculations. the values plotted are geometric mean normalized standard deviations for temperature (humidity values are indistinguishable), sulfur dioxide and small particles (in the two size bands used here, 0.4 - 0.7 μm and 0.7 - 1.1 μm diameter). As high-frequency noise is rejected by smoothing with increasing time constant, the effect on particle standard deviations is seen to be greatest. At the other extreme, the effect on temperature (and humidity) standard deviations is the least among the presently observed quantities. This is seen as a direct consequence of the ease with which temperature and humidity records can be obtained using modern sensors. It should be noted that for particles the problem is exacerbated by effects associated with poor counting statistics. The roll-off associated with the sulfur dioxide data is less than that associated with the measurement of particle concentration, but greater than that for the meteorological variables. In this context, the use of covariances (with w) instead of standard deviations as indicators of total turbulent transport seems especially attractive, since the influence of high frequency noise is then minimized.

Figure 2 illustrates the ability of the similarity methods advocated here to provide accurate estimates of vertical fluxes. For purposes of illustration, Figure 2 plots estimated latent heat fluxes, LE, derived from using the most smoothed data (30-second time constant) used in the generation of Table 1, against the actual values measured by eddy correlation.

It is obvious that the use of variance data as a basis for computations using the similarity/heat-budget approach leads to potential difficulties concerning the direction of the flux, precisely as in the case of direct analysis of variance in conventional meteorological applications. An alternative method is presently being evaluated, in which the standard deviations in Equations (3)-(7) are replaced by covariances computed using some other, well-measured meteorological variable. In this way, random noise should be rejected, since by definition it will be uncorrelated with any other signal. Furthermore, information on the sign of the vertical flux will be retained.

Acknowledgement

This work was supported by the U.S. Environmental Protection Agency as a contribution to the National Acid Precipitation Assessment Program.

Reference

Hicks, B. B., 1979: Some Micrometeorological Methods for Measuring Dry Deposition Rates, AICHE Symposium Series, 75, Number 188, 187 - 190.

TABLE 1. Examples of data generated by a test of the theory of similarity methods for deducing pollutant deposition from radiation data and heat budget considerations, using slow-responding pollution sensors. All data are for 30-minute runs, above a forest canopy. Data are quoted for 1, 3, 10, and 30 second response time sensors. Units for global (R_g) net radiation (R_n), sensible heat flux (H) and latent heat flux (LE) are W/m^{-2}. All other quantities are normalized to unity for "perfect" sensors. Fluxes F1, F2, and F3 are of SO_2, small particles (0.4 - 0.7 μm diameter), and larger particles (0.7 - 1.1 μm), respectively. The remaining quantities are standard deviations, also normalized.

	H	LE	F1	F2	F3	ST	Sq	S1	S2	S3
1500 - 1530, 2 May 1983, R_g = 775, R_n = 540										
	224	279	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
1 sec	220	274	1.00	1.00	1.00	.99	.99	1.00	.99	.98
3 sec	205	259	.99	1.00	1.00	.98	.98	1.00	.99	.95
10 sec	169	228	.97	.94	.92	.94	.94	.99	.97	.91
30 sec	71	149	.90	.84	.80	.85	.86	.96	.95	.87
1530 - 1600, 2 May 1983, R_g = 640, R_n = 465										
	245	205	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
1 sec	242	202	.99	1.00	1.03	.98	.99	.99	.94	.94
3 sec	231	192	.97	.83	1.27	.96	.96	.97	.85	.85
10 sec	197	160	.92	.83	.92	.91	.92	.95	.69	.72
30 sec	151	119	.77	.83	.89	.84	.84	.90	.58	.59
1600 - 1630, 2 May 1983 R_g = 576, R_n = 385										
	166	124	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
1 sec	162	120	1.00	.98	.92	.98	.99	.94	.94	.94
3 sec	147	108	1.01	.84	.60	.96	.96	.88	.84	.84
10 sec	108	78	.88	.66	.27	.91	.91	.78	.66	.69
30 sec	62	44	.33	.79	.21	.82	.82	.70	.51	.56
1630 - 1700, 2 May 1983 R_g = 473, R_n = 302										
	136	92	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
1 sec	132	88	.91	.89	.99	.98	.98	.94	.89	.95
3 sec	121	80	.71	1.20	.87	.96	.96	.89	.84	.85
10 sec	95	60	.63	.21	.63	.90	.90	.81	.69	.72
30 sec	51	31	.15	1.01	.48	.81	.81	.71	.52	.56
1700 - 1730, 2 May 1983 R_g = 352, R_n = 196										
	109	82	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
1 sec	108	80	.99	.74	.83	.98	.99	.95	.94	.94
3 sec	99	74	.95	1.02	.65	.96	.96	.89	.85	.83
10 sec	79	59	.73	.38	.99	.91	.90	.78	.68	.69
30 sec	47	39	.29	-.32	1.38	.67	.83	.67	.52	.54
1730 - 1800, 2 May 1983 R_g = 243, R_n = 103										
	125	49	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
1 sec	123	47	.99	.90	1.10	.98	.96	.93	.94	.94
3 sec	114	43	.96	.96	.87	.96	.94	.87	.84	.85
10 sec	98	36	.82	.19	1.37	.91	.89	.75	.67	.69
30 sec	55	21	.57	.30	1.10	.82	.79	.62	.50	.53

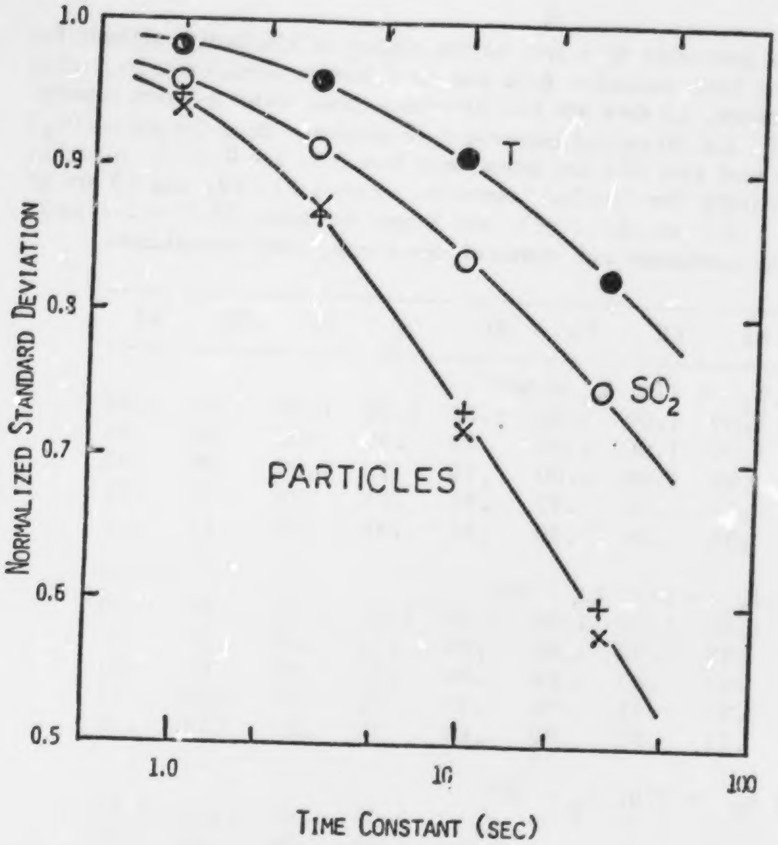


Figure 1. The effect of sampling response time on standard deviation associated with temperature (dots), sulfur dioxide (circles), and particle concentration (crosses) records. Data are normalized to values obtained from "raw" data obtained from fast-response sensors.

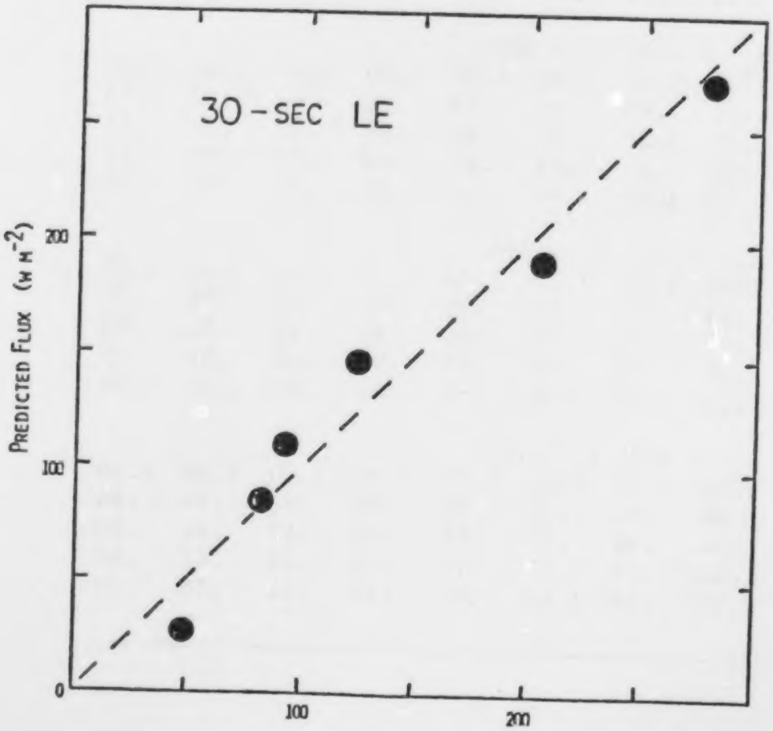


Figure 2. A comparison of latent heat fluxes derived by application of Equation (5), with direct-measurements made by eddy correlation. The total heat storage term is assumed to be a constant 10% of the net radiation.

AN EDDY ACCUMULATOR FOR DRY DEPOSITION MEASUREMENTS

R. E. Speer, T. G. Ellestad, and J. L. Durham
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

INTRODUCTION

For applications requiring measurements of the turbulent fluxes of trace gases to the earth's surface, the so-called eddy accumulation variation on conventional eddy correlation continues to offer promise, despite acknowledged technical difficulties that have so far proved prohibitive. In essence, the method bypasses the usual requirement for a rapidly-responding sensor of the atmospheric concentration of the trace gas of interest. Instead, a fast-response pumping system is used to sample air at a rate proportional to the vertical velocity. Two samples are then accumulated, one corresponding to updrafts and the other to downdrafts. The differences in average concentrations accumulated in these two independent samples is directly related to the conventional eddy flux. The method has been described in detail elsewhere (e.g. Hales and Horst, 1974; Desjardins, 1977; Hicks and McMillen, 1985). If applied correctly, the eddy accumulation technique would have the same limitations as conventional eddy correlation, but would eliminate the need for two signals to be multiplied together.

Eddy accumulation has had many strong advocates, especially in the context of measuring dry deposition, but success has been so elusive that there are few references in the open literature. Nevertheless, a review of existing and potential methods for measuring dry deposition by Hicks et al. (1980) identified eddy accumulation as a technique of special promise for measuring dry deposition. A computer simulation of the method (Hicks and McMillen, 1985) led to the identification of several major problems, each technical in nature but each presently limiting the success of the method in studies of the rates of exchange of rapidly-transferring properties. In every case, the difficulties scale inversely with the deposition velocity (Vd, defined as the ratio of flux density to atmospheric concentration) of the substance being studied. Thus, it should be easier to develop an eddy accumulation system for studies of the transfer of rapidly-deposited substances such as nitric acid vapor (Vd typically 2-5 cm/s) than it would be for a slowly-depositing substance like ozone (Vd rarely above 1 cm/s).

THEORY

Eddy accumulation separates the flux relation, $F = \overline{w'C}$, into an up and a down portion,

$$F = (\overline{w'C})_u - (\overline{w'C})_d.$$

Ideally, the sample flow rate f = Aw', and

$$F = 1/A\ [(\overline{fC})_u - (\overline{fC})_d]$$

$$F = \Delta M/AT$$

where ΔM = difference in collected sample masses, M_u and Md and T is the total sample time. In reality f = Aw' + B and is different for up and down:

$$F = 1/A_u[\overline{(f-B_u)C}]_u - 1/A_d[\overline{(f-B_d)C}]_d$$

$$F = (M_u/A_u)(1/T - B_u/V_u) - (M_d/A_d)(1/T - B_d/V_d)$$

where V_u and V_d are sample volumes and $\overline{C} = M/V$.

SYSTEM DESCRIPTION

A general block diagram of a prototype eddy accumulation field system that is under development is shown in Figure 1. In its initial configuration, the vertical component of the wind velocity is sensed with a propeller anemometer whose output is a DC voltage proportional to the wind velocity component parallel to the propeller axis. The mean component, w, of this signal is removed by a high-pass filter with a time constant of 100 s, leaving only the variable component, w'. A polarity detector uses the signal Aw' to control a solenoid valve with a switching time of 10 ms to select the appropriate collector for sampling.

The absolute value, |Aw'| of the signal is used to control the sample flow rate, using three linked devices: an MKS Model 250A flow controller, an MKS Model 251-20000SP flow control valve, and a Thermo-Systems Model 2234 mass flow sensor, with a model 67 signal linearizer, as a flowmeter unit. The flowmeter is rated at 100 L min^{-1} with a response time of

1 ms, the control valve at 20 L min^{-1} with a response time of 10 ms. The flow controller follows the varying $|Aw'|$ signal and attempts to maintain a sample flow rate proportional to the signal and thus proportional to the vertical wind velocity by continuously reading the flow rate and adjusting the control valve for zero error signal (Figure 2).

The valves, flow sensor and related hardware are mounted on an instrument tower during field operation and are connected by signal cables to a remote electronics package, which is kept in a controlled environment to minimize temperature drifts. The flow rate signal is integrated to determine the actual volume of air sampled by each sampler, permitting corrections to be made for unequal sample volumes.

PERFORMANCE TESTS

A DC linearity bench test was performed. A range of voltages from a precision DC voltage source equivalent to w' from 0.025 to 2.5 m s^{-1} was supplied to the controller (point w, Figure 1) but with the high-pass filter's capacitor short-circuited; the resulting flow rate signal was measured (at point y, Figure 1). The average flow rate deviation from linearity was equivalent to an input of 0.002 m s^{-1} of w. At the vertical velocity threshold of 0.025 m s^{-1}, this would imply a relative error of 8%.

The frequency response of the combined controller electronics and pneumatic system was determined in laboratory and field tests. These tests consisted of comparing the flow rate signal (point y, Figure 1) with the input signal (point w, Fig. 1) to the flow controller. The response of propeller anemometers as sensors of vertical wind eddies has been dealt with previously (Hicks, 1972; Gill, 1975).

The high-frequency performance of the system operated in field conditions was tested using spectral analysis of recorded flow rate signals (Otnes and Enochson, 1972). Typical sections of records (102.6 duration) were digitized at 20 Hz and analyzed using a fast Fourier transform program. Figure 3 illustrates the results, after application of running-mean smoothing to the raw products.

The frequencies of atmospheric turbulence that are associated with the daytime vertical fluxes of materials lie mainly between normalized frequencies, $f = nz/u$, of about 0.001 to about 2.0, where n = cyclic frequency (Hz), z = height and u = mean horizontal wind velocity (Kaimal, 1973; Kaimal, et al., 1973). It appears that the eddy accumulator's linearity and frequency response should be reasonably adequate under most atmospheric conditions according to Figure 3.

FIELD TESTS

Table 1 gives some of the species that we have been measuring or plan to measure with the eddy accumulator. At the present time we are concentrating on water vapor since it has a high flux rate, can be analyzed with high precision and can be used as a check on the eddy accumulator's performance by comparing with flux values obtained by other independent means.

TABLE 1. SAMPLE ANALYSIS

Species	Collection Medium	Analysis Method
H_2O	Molecular sieve	Weighing
SO_2, NO_2	TEA impregnated filter	Ion Chrom.
Sulfate, nitrate	Nylon filter	Ion Chrom.

The results of water vapor flux measurements during the first field test are given in Speer, et. al., 1985. The results did not correlate very well with eddy correlation data from the same site and indicate that there are problems that remain to be overcome.

Samples for SO_2 have been collected during field tests but improvements in the precision of the ion chromatographic analysis, particularly in adequately resolving the small mass differences between the up and down filter samples, need to be made before these are analyzed.

FUTURE PLANS

Some changes to be made in the near future include a computer controlled system and a sonic anemometer. The computer system's software will replace functions that are being performed by analog circuitry in the present system, including control of flow rate. The sonic anemometer will improve on the propeller anemometer's slow response.

CONCLUSION

The development of the eddy accumulator should be considered at the present time as a work in progress. Significant steps have been made toward the goal of a working system, mainly in developing a fast response sampling apparatus, but other obstacles need to be overcome. Effort will be concentrated on identifying the sources of errors and on making the planned improvements mentioned previously in this report.

REFERENCES

Desjardins, R. L., 1977; Description and Evaluation of a Sensible Heat Flux Detector, Boundary-Layer Meteorol., 11, 147-154.

Gill, G. C., 1975; Development and Use of the Gill UVW Anemometer, Boundary-Layer Meteor., 8, pp. 475-495.

Hales, J. M., and T. W. Horst, 1974; A Flux Meter for Direct Field Measurement of Deposition and Resuspension Rates, In: Pacific Northwest Laboratory Annual Report for 1973, USAEC/DBER, Part 3, 176-178.

Hicks, B. B., 1972; Propellor Anemometers as Sensors of Atmospheric Turbulence, Boundary-Layer Meteor., 3, pp. 214-228.

Hicks, B. B. and R. T. McMillen, 1985; A simulation of the eddy accumulator method for measuring pollutant fluxes, J. Climat. and Appl. Meteor., 23, pp. 637-643.

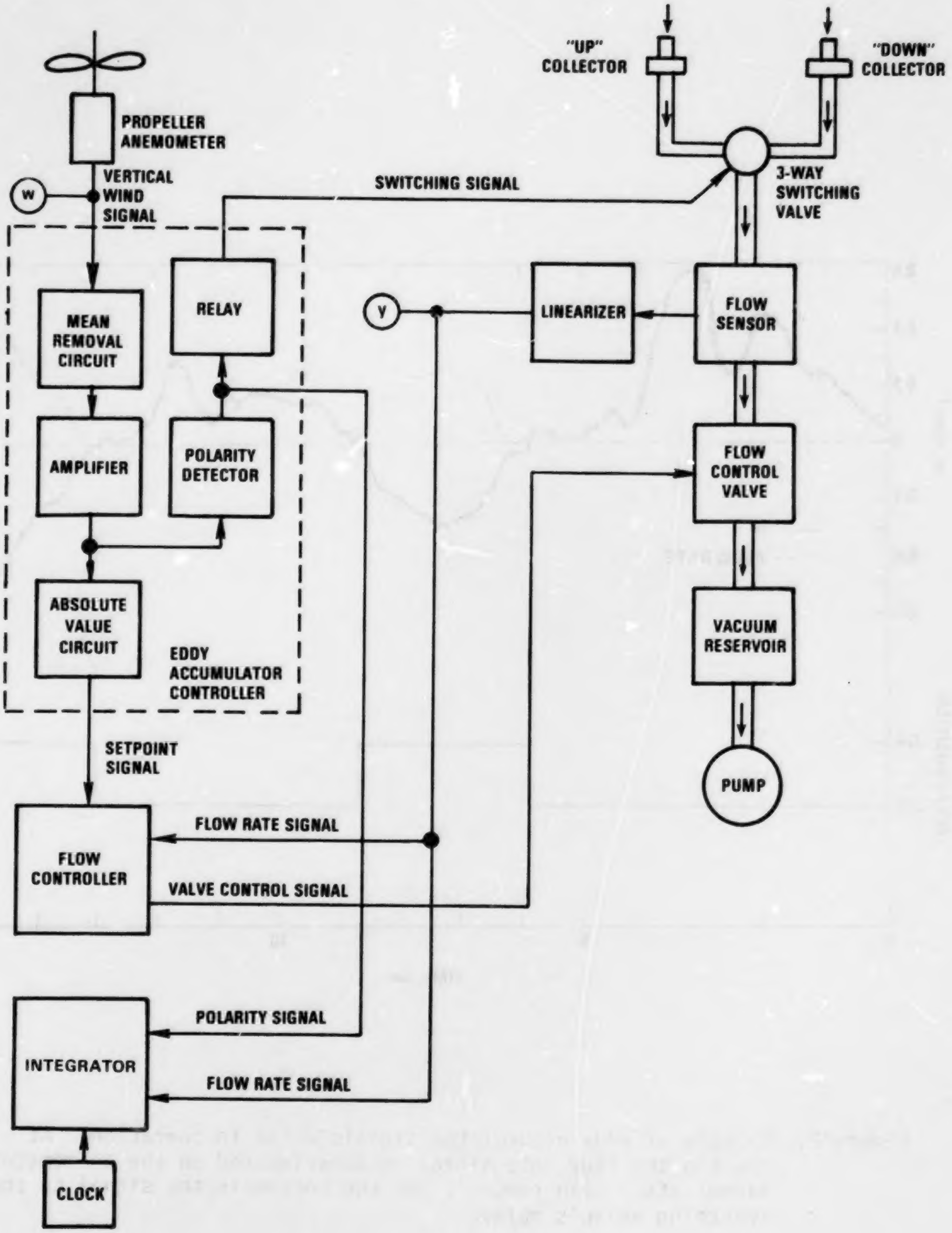
Hicks, B. B., M. L. Wesely, and J. L. Durham, 1980; Critique of Methods to Measure Dry Deposition: Workshop Summary, EPA Report EPA-600/9-80-050, NTIS Publication PB81-126443.

Kaimal, J. C., 1973; Turbulence Spectra, Length Scales and Structure Parameters in the Stable Surface Layer, Boundary-Layer Meteor., 4, pp. 289-309.

Kaimal, J. C., J. C. Wyngaard, Y. Izumi, and O. R. Cote, 1972; Spectral Characteristics of Surface-Layer Turbulence, Quart. J. of the Royal Meteor. Soc., 98, pp. 563-589.

Otnes, R. K. and Enochson, 1972; Digital Time Series Analysis, (Wiley-Interscience, New York).

Speer, R. E., K. A. Peterson, T. G. Ellestad, and J. L. Durham, 1985; Test of a Prototype Eddy Accumulator for Measuring Atmospheric Vertical Fluxes of Water Vapor and Particulate Sulfate, J. Geophys. Res., 90, pp. 2119-2122.



"UP" COLLECTOR
"DOWN" COLLECTOR
PROPELLER ANEMOMETER
VERTICAL WIND SIGNAL
w
SWITCHING SIGNAL
3-WAY SWITCHING VALVE
MEAN REMOVAL CIRCUIT
RELAY
y
LINEARIZER
FLOW SENSOR
AMPLIFIER
POLARITY DETECTOR
FLOW CONTROL VALVE
ABSOLUTE VALUE CIRCUIT
EDDY ACCUMULATOR CONTROLLER
VACUUM RESERVOIR
SETPOINT SIGNAL
PUMP
FLOW CONTROLLER
FLOW RATE SIGNAL
VALVE CONTROL SIGNAL
INTEGRATOR
POLARITY SIGNAL
FLOW RATE SIGNAL
CLOCK

Figure 1. Block diagram of the eddy accumulator system. Signals at points w and y were the input and output signals, respectively, for the performance tests.

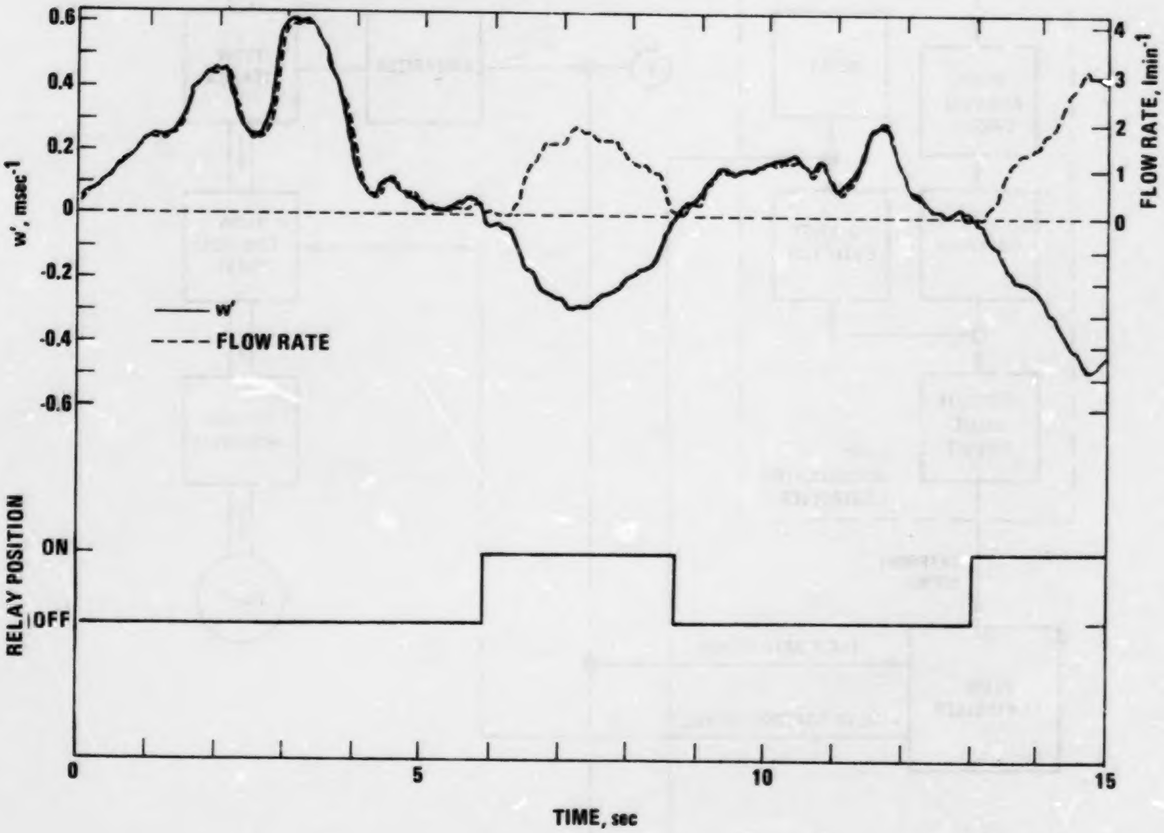


Figure 2. Example of eddy accumulator signals while in operation. At the top the flow rate signal is superimposed on the anemometer signal after mean removal. At the bottom is the signal to the switching valve's relay.

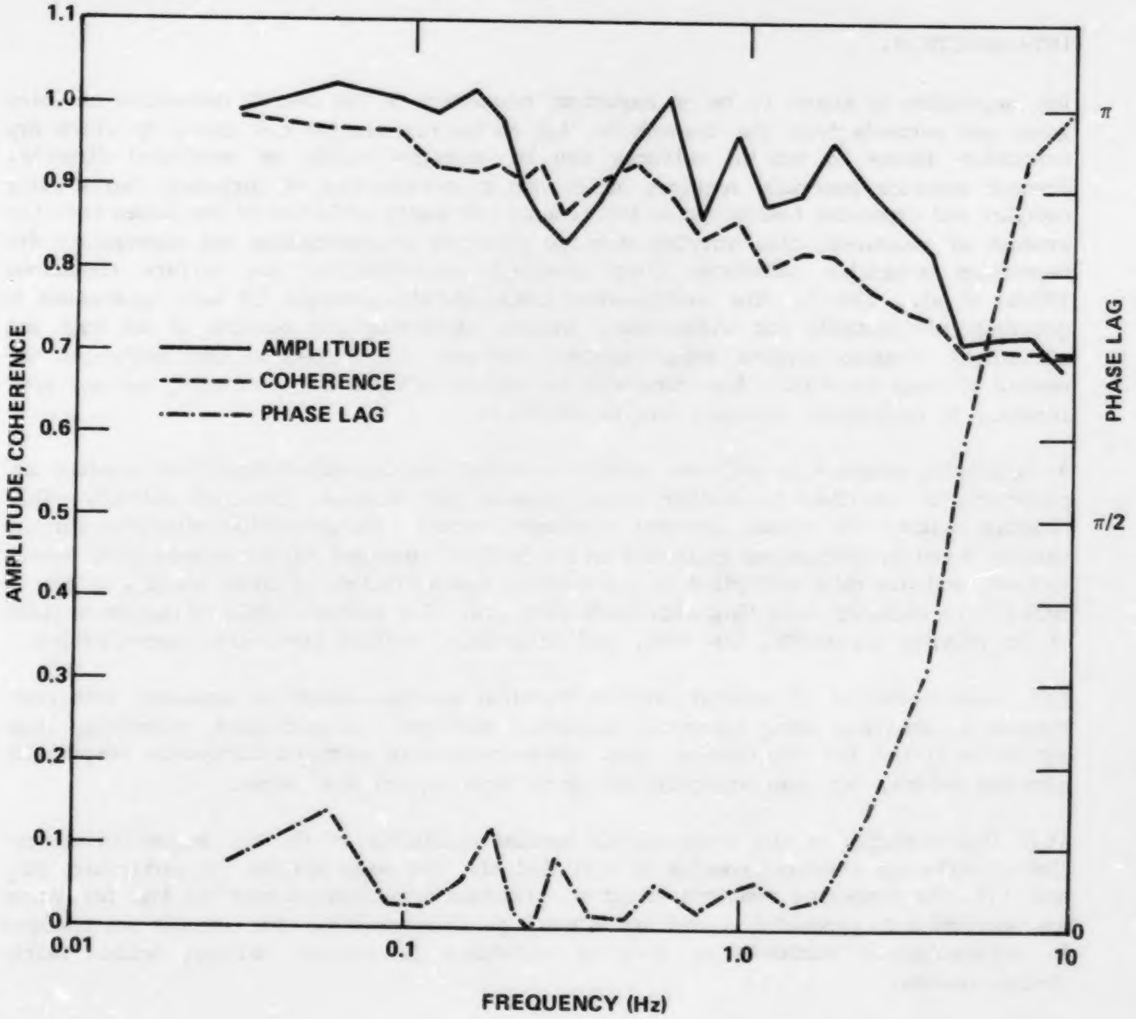


Figure 3. Frequency response of the eddy accumulator's flow system from spectral analysis of flow rate vs. input signal while operating under field conditions.

A PROTOTYPE CONCENTRATION ACCUMULATION APPARATUS FOR DETERMINING TIME-AVERAGED DRY DEPOSITION OF GASEOUS POLLUTANTS

B. B. Hicks, R. P. Hosker, Jr., and Ma, Guo-Jun*

Atmospheric Turbulence and Diffusion Division
NOAA/ERL/Air Resources Laboratory
Oak Ridge, TN 37831

INTRODUCTION.

Dry deposition is known to be an important component in the overall deposition of trace gases and aerosols from the atmosphere, but no instrumentation now exists by which dry deposition fluxes to natural surfaces can be measured easily or monitored directly. Present practice generally requires either direct measurement of turbulent fluxes using complex and expensive fast-response instruments, or makes estimates of the fluxes from the product of measured, time-varying airborne pollutant concentrations and appropriate dry deposition velocities calculated from observed meteorological and surface conditions (Hicks et al., 1985). The sophisticated instrumentation needed for both approaches is generally not suitable for widespread, routine monitoring use because of its cost and technically complex support requirements. Because dry deposition flux estimates are needed at many locations, less expensive techniques suitable for monitoring use are preferable, if reasonable accuracy can be obtained.

A monitoring program to estimate weekly-averaged dry deposition fluxes of selected air pollutants is described in another paper (Hosker and Womack, this symposium). That program follows the second approach mentioned above: dry deposition velocities for the various chemical species are estimated on the basis of recorded micrometeorological observations, and are then multiplied by the average concentrations of those species as determined from constant mass flow filterpack samplers. The method, while attractive because of its relative simplicity, low cost, and reliability, suffers from some uncertainties.

(a) Concentrations of several critical chemical species cannot be measured with confidence at all times using filterpack collection methods. In particular, techniques must yet be perfected for determining trace concentrations of nitrogen compounds (especially nitrogen oxides, but also ammonia and nitric acid vapor) and ozone.

(b) Understanding of the temporal and spatial variability of the dry deposition velocities of different chemical species is still limited. For some species (in particular, SO_2 and O_3), the concerted research effort by numerous investigators over the last few years has succeeded in producing deposition velocity parameterizations that account for changes in meteorological variables as well as variations in surface biology, within fairly limited bounds.

However, knowledge of the deposition of even the better understood trace gases is still lacking for many natural surfaces, and is unavailable for the deposition of other trace species to nearly all vegetated surfaces. Hicks et al. (1985) describe the relevant parameterizations and their limitations.

(c) At any given location, both atmospheric trace species concentrations and the associated dry deposition velocities are likely to fluctuate widely with time. This raises some question about the accuracy of average flux estimates calculated from the product of average airborne concentrations and average deposition velocities. In principle, at least, the time-average ought to be computed from the product of the fluctuating concentration and deposition velocity.

---

* Atmospheric Environment Monitoring and Research Centre, Ministry of Water Resources and Electric Power, Nanjing, Peoples' Republic of China.

The method described here is intended to sidestep the errors arising from the simple filterpack monitoring program's approximation of average fluxes by the product of average concentration and average deposition velocity. The new instrumentation will be deployed at selected locations to provide direct comparisons with the average fluxes inferred from the product of averages, with those calculated from hourly integration of deposition fluxes evaluated from higher time resolution data, and with fluxes determined from occasional eddy correlation measurements. The new technique is designed to retain the convenience of a filterpack chemical sampling system without the need for expensive and complex chemical monitors (and their required elaborate support systems), or for extensive and costly laboratory analysis. The method is somewhat similar to "eddy accumulation", as discussed by Hicks et al. (1980) and by Hicks and McMillen (1984). The new approach suggested here is therefore called "concentration accumulation".

THEORY OF OPERATION.

In the prototype dry deposition monitoring program described elsewhere, suitable micrometeorological instruments are deployed to provide the data necessary to deduce chemical species-dependent, time-varying values of dry deposition velocities at each site. In particular, wind speed, wind direction variability, air temperature, humidity, insolation, rainfall, and surface wetness are continuously monitored, and 15-min averages of these quantities are recorded. Supporting information on local surface and vegetation conditions is derived from weekly reports by site operators; these include observations of vegetative species, condition, height, leaf area index, and water availability. The formulations used to estimate dry deposition velocities for SO_2 and HNO_3 vapor from the meteorological and vegetation data are based on the resistance analog for mass transfer, as described by Hicks et al. (1985). The "concentration accumulation" method makes use of the availability of this relatively high time resolution information on dry deposition velocity as follows.

Consider a sampling system which aspirates an air/trace-pollutant mixture. The total mass M passing through the system in some time interval T is

$$M = \int_0^T (\rho_a + C)\ V\ A\ dt \qquad (1)$$

where ρ_a is the local air density, C is the airborne pollutant concentration, and VA is the volume flow rate through the sampler tube. Similarly, the mass of pollutant M_p passing through the system during that same time interval is

$$M_p = \int_0^T C\ V\ A\ dt \qquad (2)$$

Assume all (or at least a well-known fraction) of the pollutant is captured on a filter.

The key step is to adjust the mass flow rate through the sampler so that it is directly proportional to the pollutant's dry deposition velocity V_D, as calculated from the ambient meteorological and surface conditions. That is, set

$$(\rho_a + C)\ V\ A\ =\ K\ V_D \tag{3}$$

Then, for low ambient concentrations,

$$M_p \cong \frac{K}{\overline{\rho}_a} \int_0^T V_D\ C\ dt. \tag{4}$$

The average dry deposition flux $\overline{F}$ is

$$\overline{F} = \frac{1}{T} \int_0^T V_D\ C\ dt \tag{5}$$

so there is a direct relation between the dry deposition flux and the amount of pollutant captured by the filterpack sampler:

$$M_p \cong \frac{K\ T}{\overline{\rho}_a}\ \overline{F}. \tag{6}$$

The total mass of air and pollutant passing through the system is just

$$M = \int_0^T (\rho_a + C)\ V\ A\ dt = \int_0^T K\ V_D\ dt, \tag{7}$$

or

$$M = K\ T\ \overline{V}_D, \tag{8}$$

where $\overline{V}_D$ is the average dry deposition velocity over the interval T. Hence the average dry deposition flux can be determined from Equations (6) and (8) as

$$\overline{F} \cong \frac{\overline{\rho}_a\ \overline{V}_D}{M}\ M_p. \tag{9}$$

The average air density and average dry deposition velocity can be evaluated from continuously monitored meteorological and surface condition data, and the total mass passing through the system can be measured. The dry deposition flux is then simply proportional to the mass of pollutant collected on the filter. The sampler proportionality constant K can be evaluated from Equation (8), if desired.

SYSTEM CONFIGURATION.

A simple apparatus has been developed to use this concentration accumulation concept. The prototype system was designed to be low in cost, reliable, and compatible with commonly available meteorological equipment. A block diagram of the system is shown in Figure 1. Meteorological data from an array of instruments are scaled by special circuitry and sampled by an independently scanning eight channel analog-to-digital (A to D) converter board. An inexpensive "home" computer acquires the digital data from the A to D circuitry, converts the values into engineering units, and calculates time averages of each quantity, along with certain important statistical quantities. The averaging period is selectable, but is typically 15 minutes. The average values are then used in an algorithm based on the resistance analog to mass transfer to calculate the local dry deposition velocity for a particular air pollutant -- typically HNO_3 or SO_2. The meteorological data and the estimated dry deposition velocity are recorded on cassette tape, together with the date and time. A digital-to-analog (D to A) converter provides an output signal proportional to the estimated V_D. This signal is used to modulate the flow rate through an electronic mass flow controller in a filterpack sampling system. The flow rate is also monitored and recorded by the computer so that the total mass flow through the system is known. At the end of the averaging period, a new dry deposition velocity is calculated on the basis of the average meteorological and surface conditions during that period, and the flow rate through the filterpack system is readjusted. Meteorological data collection and concentration sampling continue for one week, just as in the constant flow rate filterpack monitoring system described separately. An inexpensive DC to AC power inverter is operated by a continuously charged 12V battery to protect the computer against power line interruptions. The filterpack unit is the same as that described (Hosker and Womack, this symposium) for the constant flow system. Figure 2 is a photograph of the prototype system.

PRESENT STATUS.

The prototype data acquisition, computational, and controller system has been completed and tested in the laboratory, and is ready for field use. Figure 3 shows typical dry deposition velocity estimates for HNO_3 over four days last spring; these are taken from strip chart recordings of the D to A converter output that would be used in practice to modulate the mass flow rate through the filterpack sampler. The diurnal cycle is clear. The rather different appearance on May 21 is due to the passage of a cold front, with strong winds and turbulence in the early evening.

It is planned to install the concentration accumulation system at the Oak Ridge "core" research site this summer, so that comparisons can be made with flux estimates produced by other systems. We expect to construct two more of these new systems for installation at other "core" sites. Present plans are to collect data at three sites for six to twelve months, and compare the results to direct eddy flux measurements, to continuous monitoring inferential results, and to standard filterpack monitoring results. The outcome will be presented in about a year.

REFERENCES.

Hicks, B.B., M.L. Wesely, and J.L. Durham, 1980: Critique of Methods to Measure Dry Deposition. U.S. EPA workshop summary. Avail. NTIS as PB81-126443.

Hicks, B.B., and R.T. McMillen, 1984: A simulation of the eddy accumulation method for measuring pollutant fluxes. J. Clim. Appl. Meteorol. 23 (4), 637-643.

Hicks, B.B., D.D. Baldocchi, R.P. Hosker, Jr., B.A. Hutchison, D.R. Matt, R.T. McMillen, and L.C. Satterfield, 1985: On the Use of Monitored Air Concentrations to Infer Dry Deposition. NOAA Tech. Memo. ERL-ARL- (in press), ATDL contrib. #84/24.

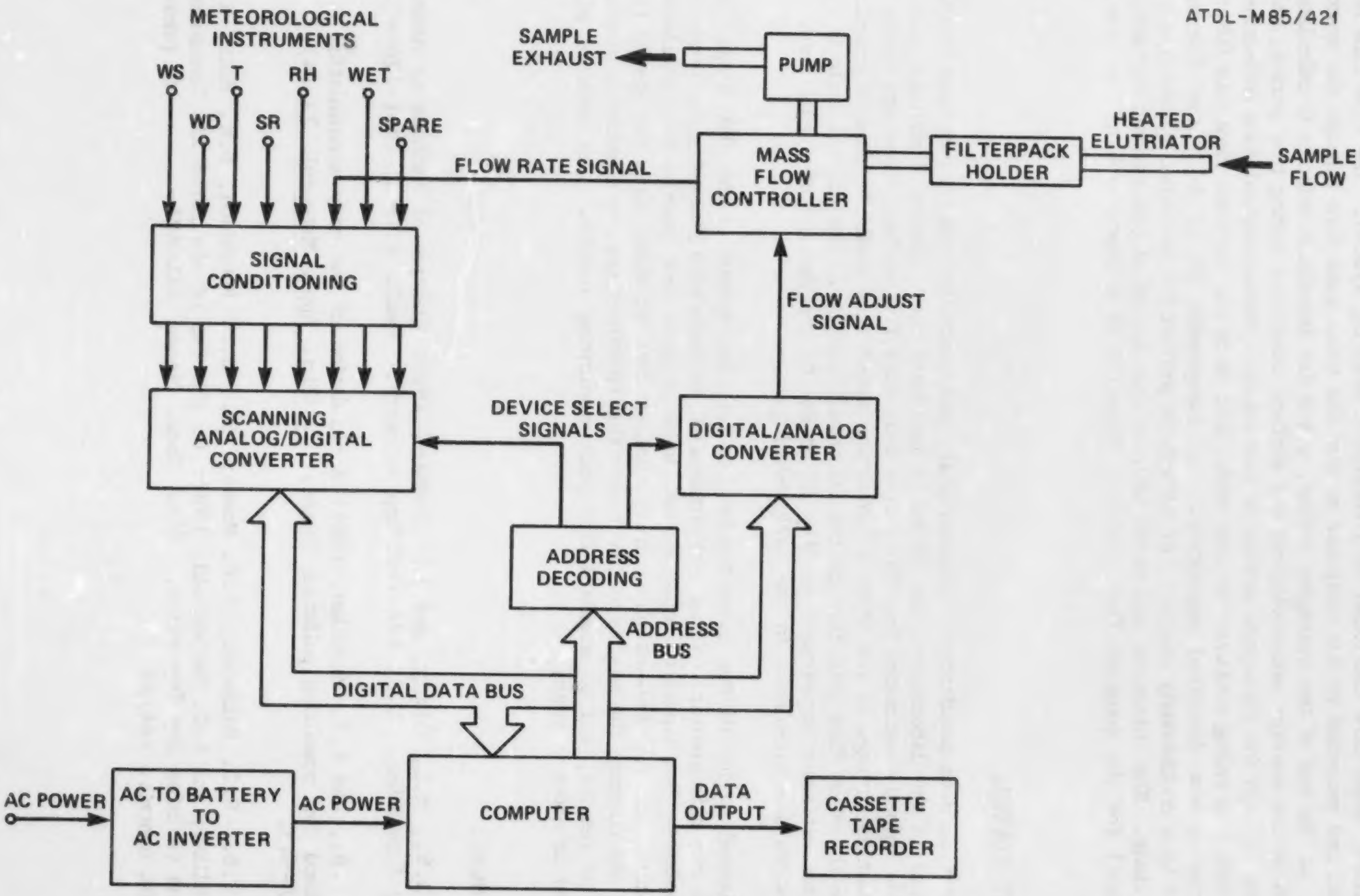

ATDL-M85/421
METEOROLOGICAL INSTRUMENTS
WS
WD
T
SR
RH
WET
SPARE
SAMPLE EXHAUST
PUMP
FLOW RATE SIGNAL
MASS FLOW CONTROLLER
FILTERPACK HOLDER
HEATED ELUTRIATOR
SAMPLE FLOW
SIGNAL CONDITIONING
FLOW ADJUST SIGNAL
SCANNING ANALOG/DIGITAL CONVERTER
DEVICE SELECT SIGNALS
DIGITAL/ANALOG CONVERTER
ADDRESS DECODING
ADDRESS BUS
DIGITAL DATA BUS
AC POWER
AC TO BATTERY TO AC INVERTER
AC POWER
COMPUTER
DATA OUTPUT
CASSETTE TAPE RECORDER

Figure 1. Schematic of prototype concentration accumulation system. Flow rate through the filterpack sampler is modulated according to the dry deposition velocity, as calculated on the basis of the meteorological and surface conditions.

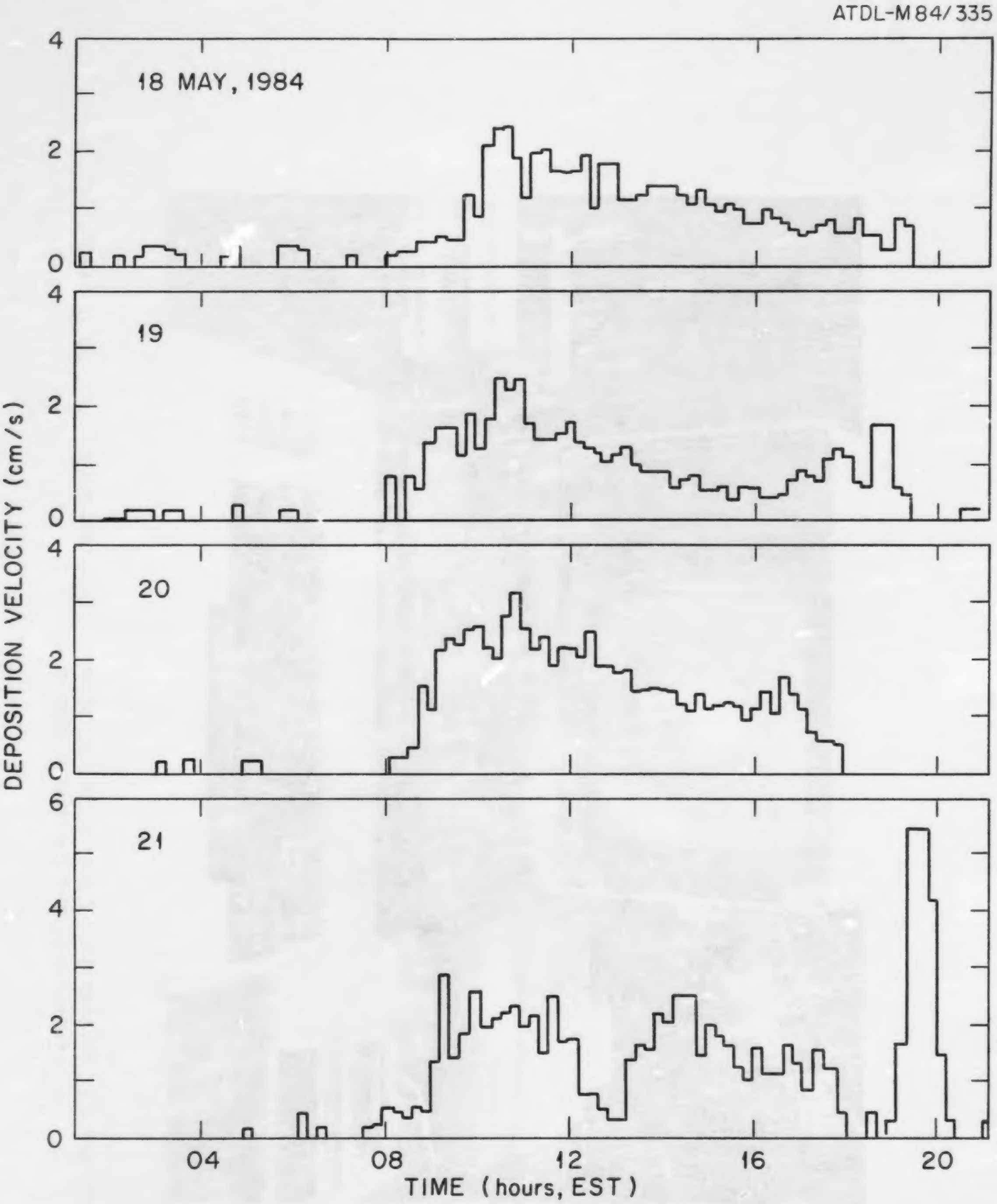


Figure 3. Dry deposition velocity estimate for HNO_3 over several days, using prototype system. The mass flow rate through the filterpack would be varied according to this signal.

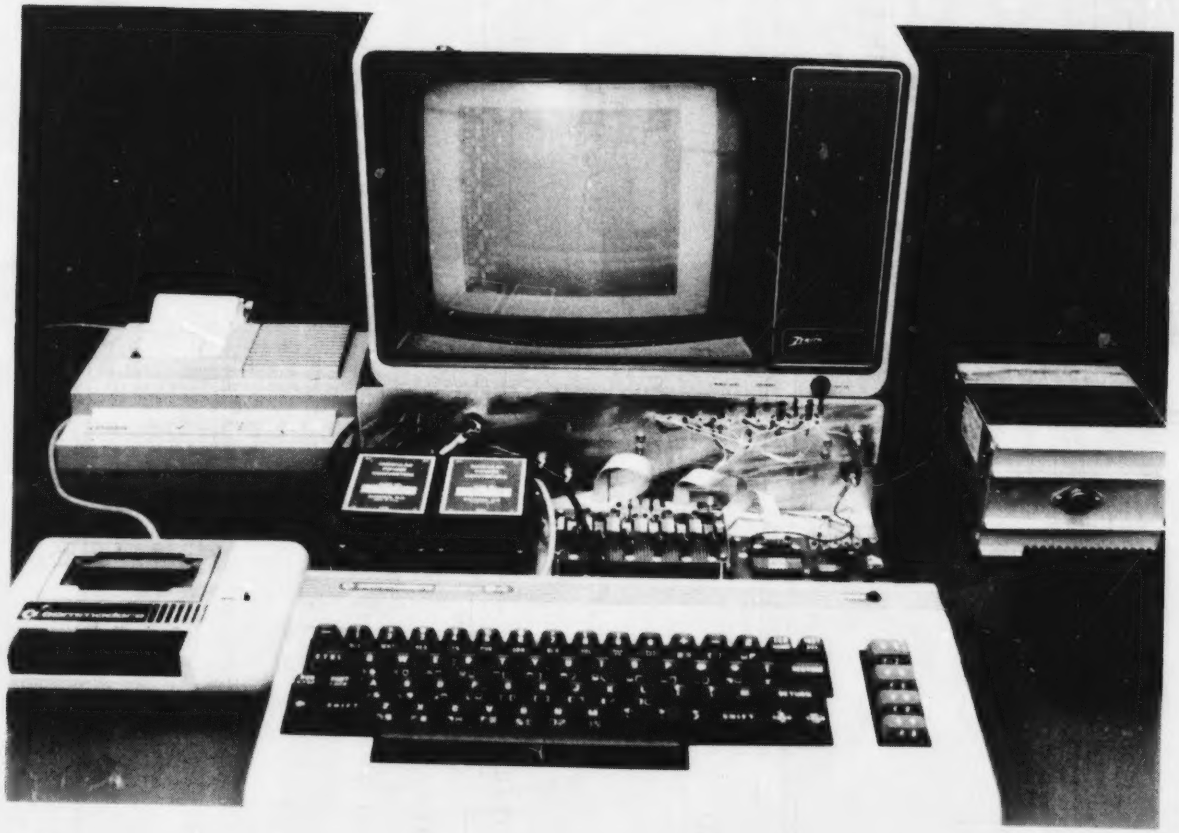


Figure 2. Photograph of prototype concentration accumulation data acquisition, processing, and recording system.

SIMPLE METEOROLOGICAL AND CHEMICAL FILTERPACK MONITORING SYSTEM FOR ESTIMATING DRY DEPOSITION OF GASEOUS POLLUTANTS.

R. P. Hosker and J. D. Womack*

Atmospheric Turbulence and Diffusion Division
NOAA/ERL/Air Resources Laboratory
Oak Ridge, TN 37831

INTRODUCTION.

The equipment and procedures described here are in use in a prototype network for long-term monitoring of dry deposition of gaseous (and later, particulate) pollutants. At this time, the method is limited to SO_2 and HNO_3 vapor. The method is only one of several being tested and compared at a sub-network of "core" research sites. The goal of this work is to determine dry deposition spatial distributions and temporal trends with the same statistical confidence as for the wet deposition case.

Dry deposition fluxes can be evaluated from meteorological data and concentration measurements by several techniques. Most of these are too complex or too operationally demanding to be suitable for use in routine monitoring applications. However, so-called inferential methods appear promising. Inferential methods infer the dry deposition velocity V_D of a pollutant from meteorological and local surface condition data; concentrations C of air pollutants are measured directly. The dry deposition flux is then estimated from the product of V_D and C for each pollutant. Errors can arise from inaccuracies or inadequacies in the procedure used to infer V_D, and from errors in approximating the time average of products by the product of averages. However, the method is suitable for long-term monitoring if these errors can be reduced or quantified. The inferential method is the basis for the system described here.

The measurement philosophy is to measure appropriate physical, chemical, and biological variables with enough temporal resolution to compute weekly average dry deposition fluxes at a large number of sites. This monitoring network is supported by a subset of research-grade stations to provide details of distributions, episodes, and deposition processes; these are used to improve the techniques applied to the less exact but more extensive array of filterpack monitoring stations.

It is difficult to measure low concentrations of pollutants with good time resolution using inexpensive apparatus. One solution is to accumulate pollutants in a filterpack sampler over some time interval, an appropriate averaging time must be selected. The equations for estimating the average dry deposition flux $\overline{F}$ can be successively approximated:

$$\overline{F} = \frac{1}{T}\int_0^T V_D * C \, dt \qquad (1)$$

---

* Affiliated with Oak Ridge Associated Universities.

$$\cong \frac{1}{N}\sum_{i=1}^{N} V_D(t_i) * C(t_i) \qquad (2)$$

$$\cong \overline{V}_D * \overline{C}. \qquad (3)$$

How good are these various approximations? Co-location of filterpack monitoring stations and research-grade (core) measurement sites using continuous pollutant monitoring is intended to help answer this question. At present, a weekly collection schedule (average) is used.

EQUIPMENT AND OPERATION.

Figure 1 shows a diagram of a filterpack station. The computer routine used to infer the dry deposition velocity requires data on wind speed, wind direction fluctuations (σ_θ), solar radiation, temperature, relative humidity, precipitation, and local surface wetness. These data are acquired from sensors mounted at 10 m height. The sensors are sampled every 10 s by a small commercial data logger, which preprocesses the data, calculates 15 min and 60 min averages and statistics, and records the results on a cassette tape. A reference voltage checks the data logger accuracy and also the AC power line, so that power outages, which may cause erroneous temperature and humidity readings, are flagged. An active mass flow controller maintains a constant flow (3 ℓ/min) through the filterpack, regardless of the degree of filter loading; the data logger monitors the flow rate and controller voltage. A trickle-charged battery powers the data logger, to preclude battery changes and consequent reprogramming of the system. The instrument enclosure is self-insulated and weathertight, so that it can be mounted on the tower without special protection. The enclosure is heated and fan-cooled to provide reliable instrument performance. Figure 2 shows a typical system.

Figure 3 shows the filterpack assembly, a modification of the system commonly used in Canada. A weakly-heated elutriator tube removes particles and helps prevent condensation of ambient moisture on the filters. The air then flows through a Teflon particle filter (2 μm), a nylon filter to remove HNO_3, and a sodium carbonate-doped cellulose filter for collecting SO_2.

The data tape and the filters are replaced every Tuesday morning. The data tapes are returned to our laboratory where a QC screening is applied; acceptable data are then copied into desktop computer files for analysis. The filters are sent to the U.S.G.S. laboratory in Atlanta, GA for extraction and ion chromatographic analysis following a protocol designed by the EPA's ASRL/Aerosol Research Branch. Results are merged with the meteorological data, and archived. Estimates of the weekly average dry deposition velocities for HNO_3 and SO_2 are calculated using the meteorological data and observations of surface conditions, and multiplied by the measured weekly average concentrations to determine the average flux.

Additional system details may be found in Hosker and Womack (1985).

DRY DEPOSITION VELOCITY ESTIMATION.

Successful flux estimation via concentration monitoring requires the ability to infer V_D accurately from meteorological data, pollutant properties, and observations of local surface conditions and vegetation. Space precludes extensive discussion of the computational methods; see Hicks *et al.* (1985) for details. Briefly, the resistance analog is used; the total resistance to mass transfer, R_T, is given by the sum of three terms, an aerodynamic resistance to turbulent transfer, R_A, a diffusive boundary layer resistance, R_B, and a resistance to uptake by vegetation, soil, and other receptors, R_C. Thus

$$R_T = R_A + R_B + R_C \qquad (4)$$

and

$$V_D = (R_T)^{-1}. \qquad (5)$$

The aerodynamic resistance depends on the atmospheric turbulence, and may be written in terms of the stability-dependent wind profile (Wesely and Hicks, 1977):

$$R_A = (ku_*)^{-1} \; [\; \ln(z/z_0) + \psi_c(z/L) \;] \qquad (6)$$

$$\cong (\sigma_v/u_*)^2 \; (U \; \sigma_\theta^2)^{-1} \qquad (7)$$

or, in terms of the standard deviation of wind direction σ_θ,

$$R_A \cong 4 \; (U \; \sigma_\theta^2)^{-1} \quad \text{for } z/L \geq 0 \text{ (neutral and stable)} \qquad (8)$$

$$R_A \cong 9 \; (U \; \sigma_\theta^2)^{-1} \quad \text{for } z/L < 0.1 \text{ (unstable)} \qquad (9)$$

The diffusive boundary layer resistance depends both on atmospheric conditions and on pollutant characteristics. Mathematically, R_B depends on the poorly known roughness length for pollutant transfer, z_{0C}:

$$R_B = (ku_*)^{-1} \; \ln(z_0/z_{0C}), \qquad (10)$$

so an empirical expression based on numerous studies of heat transfer is used instead:

$$R_B \cong 2 \; (ku_*)^{-1} \; (Sc/Pr)^{2/3}. \qquad (11)$$

The Schmidt number Sc enters to account for the difference in heat and pollutant diffusivities.

The most complex term is the surface uptake resistance, R_C, which depends on meteorological conditions on the microscale, on pollutant characteristics, and on receptor surface characteristics. For highly reactive gases, capture can be quite efficient, so $R_C \cong 0$. Soluble gases act much like water vapor, but with an appropriately different diffusivity. Wet surfaces can be especially efficient collectors. The various biological resistances (stomatal, cuticular, mesophyll) must be estimated, and weighted by the amount of active leaf area (using the leaf area index) because multiple surfaces act in parallel. Stomatal resistance depends on available light, and hence on location in the plant canopy. Biological uptake varies with the season, and with stresses such as heat and drought. Many of these dependences are still poorly understood; a good deal of work is needed to improve this portion of the procedure to estimate V_D.

THE NETWORK.

Figure 4 shows the prototype network. Additional equipment will soon be installed in central Illinois and in northern Georgia; other sites are being considered.

To assess the adequacy of the filterpack monitoring method and to allow a steady program of improvements to the prototype computational routine for V_D, three stations are co-located with continuously monitoring stations at "core" research sites in Illinois, Pennsylvania, and Tennessee. Direct eddy correlation measurements are also made periodically at these sites, to test the other flux estimates. So-called "concentration accumulation" apparatus, described in another paper, will be added to these core sites shortly.

RESULTS AND CONCLUSIONS.

A prototype network of meteorological and chemical filterpack monitoring stations has been in operation since late summer of 1984. Meteorological and surface data are collected with 15 min time resolution and used to infer a weekly average dry deposition velocity. Weekly average SO_2 and HNO_3 vapor concentrations are obtained from the filters, using the measured flow rate. Weekly average fluxes are calculated from the product of these two terms. The adequacy of the approximation will be tested by comparison to results from higher time resolution data. Preliminary results for one month at one site are shown in Table 1; the simple result involving the product of averages is within 35% (and usually within 20%) of the average of the products from the much more complex and expensive continuous pollutant monitoring system. Additional comparisons are underway, as the data are reported to us.

ACKNOWLEDGEMENT.

This research is funded as part of the National Acid Precipitation Assessment Program by the National Oceanic and Atmospheric Administration, as part of collaborative research by NOAA, the EPA, and the U.S.G.S.

REFERENCES.

Hicks, B.B., D.D. Baldocchi, R.P. Hosker, Jr., B.A. Hutchison, D.R. Matt, R.T. McMillen, and L.C. Satterfield, 1985: On the Use of Monitored Air Concentrations to Infer Dry Deposition. NOAA Tech. Memo. ERL-ARL- (in press). ATDL contribution # 84/24.

Hosker, R.P., Jr., and J.D. Womack, 1985: Prototype Meteorological Monitoring and Filterpack Sampling Systems for Dry Deposition Measurement. NOAA Tech. Memo. ERL-ARL- (in preparation).

Wesely, M.L., and B.B. Hicks, 1977: Some factors that affect the deposition rates of sulfur dioxide and similar gases on vegetation. J. Air Poll. Cont. Assoc. 27 (11), 1110-1116.

TABLE I. Sample SO_2 deposition flux comparisons at Oak Ridge "core" site, for October, 1984.

	Average Flux (grams/sq.m/week)	
Dates	$\frac{1}{N}\sum_{i=1}^{N} V_D(t_i)* C(t_i)$	$\bar{V}_D * \bar{C}$
Oct. 1 - Oct. 8	16.7	18.8
Oct. 8 - Oct.15	30.7	32.6
Oct.15 - Oct.22	51.8	59.7
Oct.22 - Oct.29	40.2	54.4

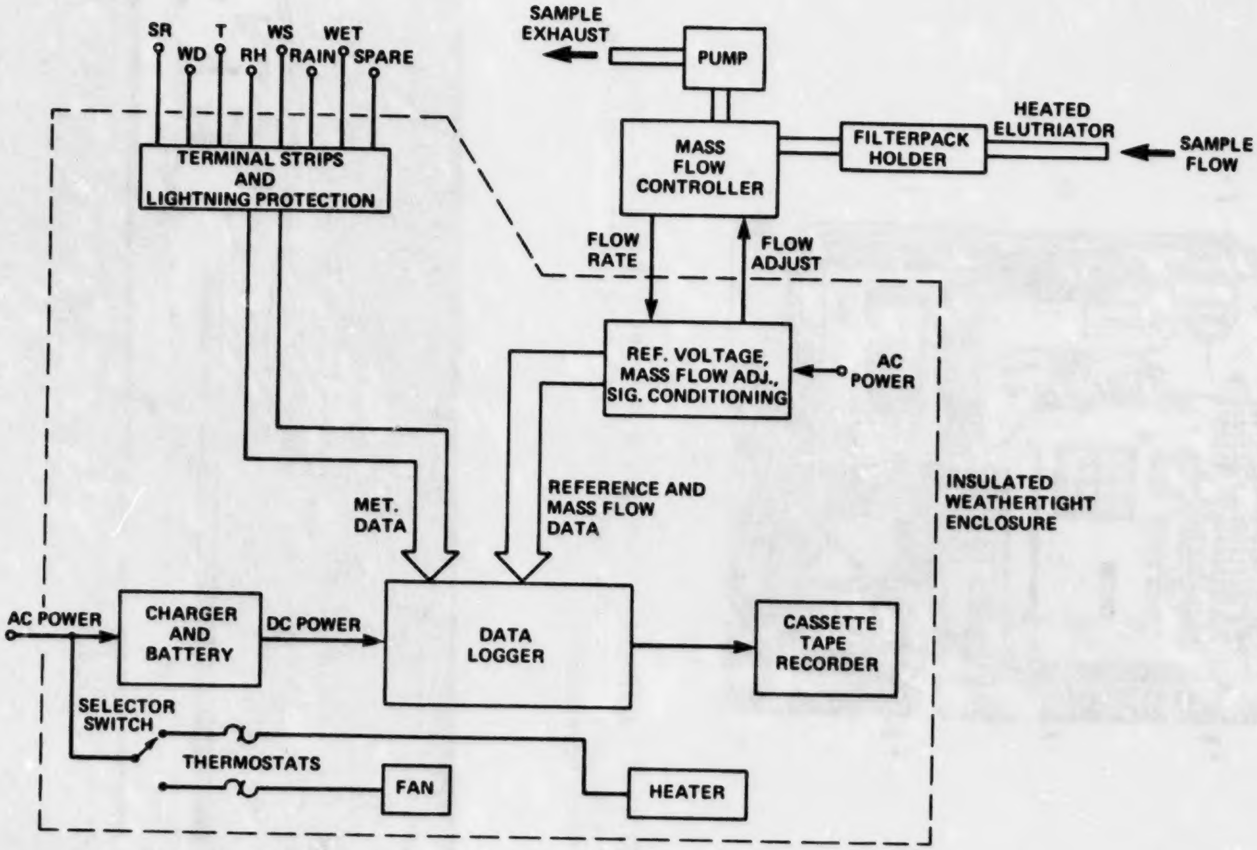

SR
WD
T
RH
WS
RAIN
WET
SPARE
TERMINAL STRIPS AND LIGHTNING PROTECTION
SAMPLE EXHAUST
PUMP
MASS FLOW CONTROLLER
FILTERPACK HOLDER
HEATED ELUTRIATOR
SAMPLE FLOW
FLOW RATE
FLOW ADJUST
REF. VOLTAGE, MASS FLOW ADJ., SIG. CONDITIONING
AC POWER
MET. DATA
REFERENCE AND MASS FLOW DATA
INSULATED WEATHERTIGHT ENCLOSURE
AC POWER
CHARGER AND BATTERY
DC POWER
DATA LOGGER
CASSETTE TAPE RECORDER
SELECTOR SWITCH
THERMOSTATS
FAN
HEATER

Figure 1. Schematic of prototype dry deposition monitoring station using constant mass flow filterpack sampler.

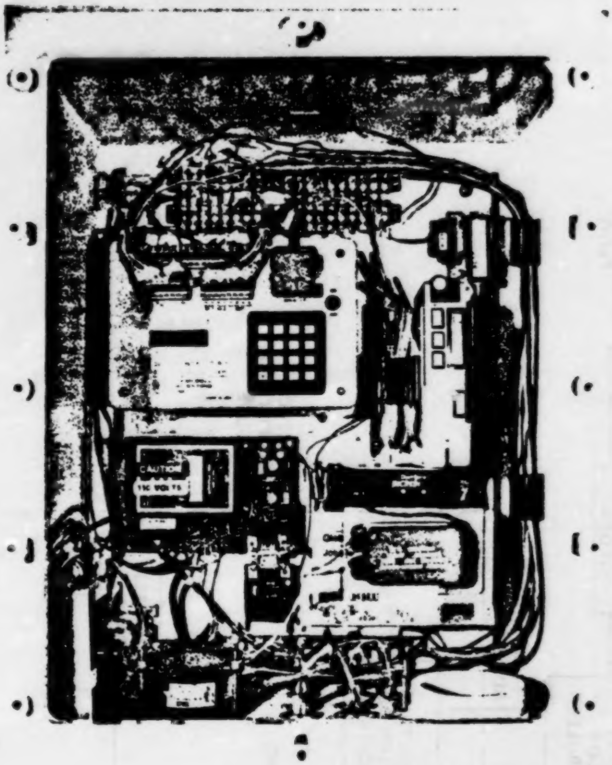


Figure 2. Typical equipment enclosure, with heater and fan, showing data logger and recorder, signal conditioning, battery and charger, and other accessories.

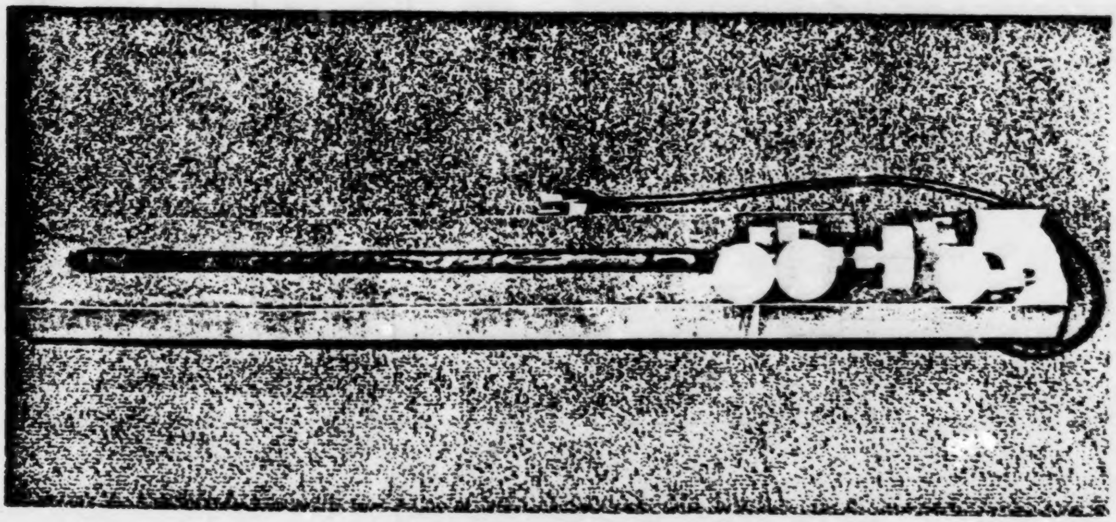


Figure 3. Filterpack assembly, with heated elutriator tube. Particle, HNO_3 and SO_2 filters are shown near holders. Units are mounted in insulated weather shield 7 m AGL.

Reproduced from best available copy.

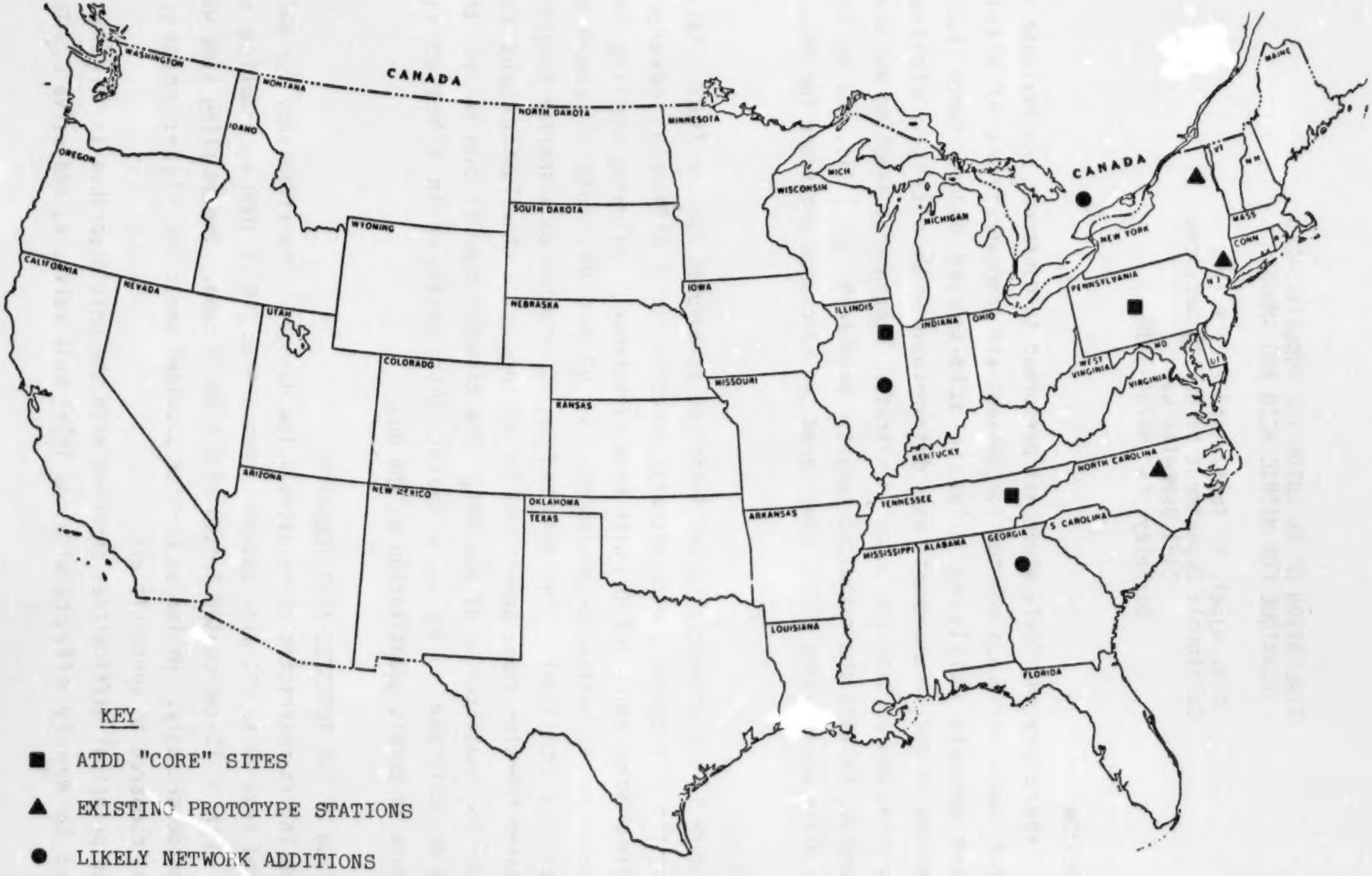

CANADA
WASHINGTON
OREGON
CALIFORNIA
NEVADA
IDAHO
MONTANA
UTAH
WYOMING
ARIZONA
COLORADO
NEW MEXICO
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
IOWA
MISSOURI
ARKANSAS
LOUISIANA
WISCONSIN
ILLINOIS
MICH
MICHIGAN
INDIANA
OHIO
KENTUCKY
TENNESSEE
MISSISSIPPI
ALABAMA
GEORGIA
FLORIDA
S CAROLINA
NORTH CAROLINA
VIRGINIA
WEST VIRGINIA
MD
PENNSYLVANIA
NEW YORK
N J
CONN
MASS
VT
N H
MAINE
KEY
■ ATDD "CORE" SITES
▲ EXISTING PROTOTYPE STATIONS
● LIKELY NETWORK ADDITIONS

Figure 4: Network of prototype dry deposition monitoring stations. Filterpack and other systems are co-located at "core" research sites.

EVALUATION OF AN AUTOMATED TUNGSTIC ACID TECHNIQUE FOR NITRIC ACID AND AMMONIA

B.R. Appel, Y. Tokiwa and E.L. Kothny
California Department of Health Services
2151 Berkeley Way
Berkeley, CA 94704-9980

INTRODUCTION

A laboratory and field study was performed to construct and evaluate an automated, semi-continuous monitor for ambient air concentrations of nitric acid and ammonia utilizing tungstic acid-coated denuder tubes (1,2). Interference in HNO_3 measurements was determined with nitrogen dioxide, nitrous acid, and particulate ammonium nitrate. Atmospheric sampling was done in Riverside, CA with the automated tungstic acid technique (TAT), and by the denuder difference method (DDM), considered the reference procedure for HNO_3.

EXPERIMENTAL

Figure 1 is a schematic of the technique as adopted for our field trials. The tungstic acid-coated preconcentrator functions as a diffusion denuder, retaining both HNO_3 and NH_3 with high efficiency. Following sampling, the preconcentrator is heated, desorbing HNO_3 as NO and NH_3 into a stream of carrier gas (helium). The desorbed NH_3 is retained on a shorter tungstic acid-coated transfer tube, permitting the NO to reach a chemiluminescent NO_x analyzer for quantitation of the HNO_3. The transfer tube is then heated, the evolved NH_3 oxidized to NO on a heated gold catalyst in a helium-air atmosphere to permit quantitation of the NH_3.

EVALUATION OF THE TUNGSTIC ACID TECHNIQUE

The TAT is restricted to relatively low dosages. The efficiency for HNO_3 decreased from 98 to 91% with dosage increase from 340 to 1000 ng sampling at 1 Lpm with a 35-cm coated length of a 4 mm ID tube. The sampling time was adjusted accordingly. Helium as carrier provided about 30% higher response for HNO_3 compared to synthetic air.

The principal difficulties observed with the unit described in Figure 1 related to memory effects with the inlet ball valve, A, and valve C. The inlet problem, sorption of HNO_3 and NH_3, was reduced by lining the Teflon ball valve with pyrex tubing. Problems with valve C developed during atmospheric sampling, apparently due to collection and subsequent slow desorption of NH_4^+ -containing materials. The resulting elevated and variable system blank prevented quantitation of atmospheric NH_3.

Concerning interference effects, NO_2 exhibited only minor interference ranging from 0.3 to 0.5% at 50% and 0% R.H., respectively. Similarly 0.1-0.2 μm NH_4NO_3 particles at dosages up to 700 ng (as NO_3^-) showed no measurable interference. Nitrous acid, however, exhibited a substantial and complex interference. Our inability to quantitate HONO has thusfar prevented assessment of its interference efficiency. Thermal desorption of WO_x coated tubes loaded with nitric acid-free HONO yielded two peaks, one of which coincided with that for HNO_3. The peak preceding HNO_3 by about 12 seconds was also observable at night and early morning during atmospheric sampling in Riverside (peak at 1.56 minute, Figure 2). Simultaneous measurements of atmospheric HONO using a UV absorption technique (3) were compared to the 1.56 min. peak areas (Figure 3). Quantitative correlation was not observed. However, when HONO was detectable by the UV method, the 1.56 min. peak was usually observed.

The precision of calibration of the TAT with HNO_3 from a permeation tube source (Metronic's Part No. 110-010-0160) at 83°C was assessed by comparing daily calibrations. For eight such calibrations, the calculated HNO_3 concentration corresponding to a typical daytime peak area exhibited a coefficient of variation of 10.5%.

The atmospheric HNO_3 results by the TAT are compared to those by the denuder difference method (4) in Figure 4. The TAT results average about 50% higher than those by the DDM. Nitrous acid interference was not a substantial contributor to the difference as evidenced by the lack of a substantial day-night effect.

ATMOSPHERIC NITRIC ACID RESULTS

Diurnal variations for two, 24-hr periods are shown in Figure 5. The decrease in HNO_3 in the interval 1300-1500 hr coincided with brief periods of rain.

STUDIES CURRENTLY IN PROGRESS

Studies continue to elucidate the cause of the difference in HNO_3 results between methods, to quantitate HONO interference and measurement, and to overcome the problems experienced in measuring NH_3. We currently are using a TAT system in which both the inlet ball valve and valve C (Figure 1) have been eliminated. An excess flow of carrier gas is vented through the sample inlet to prevent the intrusion of ambient air into the preconcentrator tube during the analytical cycle (5). The modified system will be used to sample HNO_3 and NH_3 in parallel with spectroscopic and other techniques for these atmospheric species in an interlaboratory study to be done in California.

ACKNOWLEDGEMENT

The work described herein is being sponsored by California Air Resources Board Research Division. The nitrous acid concentration measurements were provided by Dr. H. Biermann of the Statewide Air Pollution Research Center, University of California (Riverside). The assistance of Dr. A. Winer and the staff of the SAPRC is also gratefully acknowledged. Tungstic acid coated tubes were prepared by H. K. Min.

REFERENCES

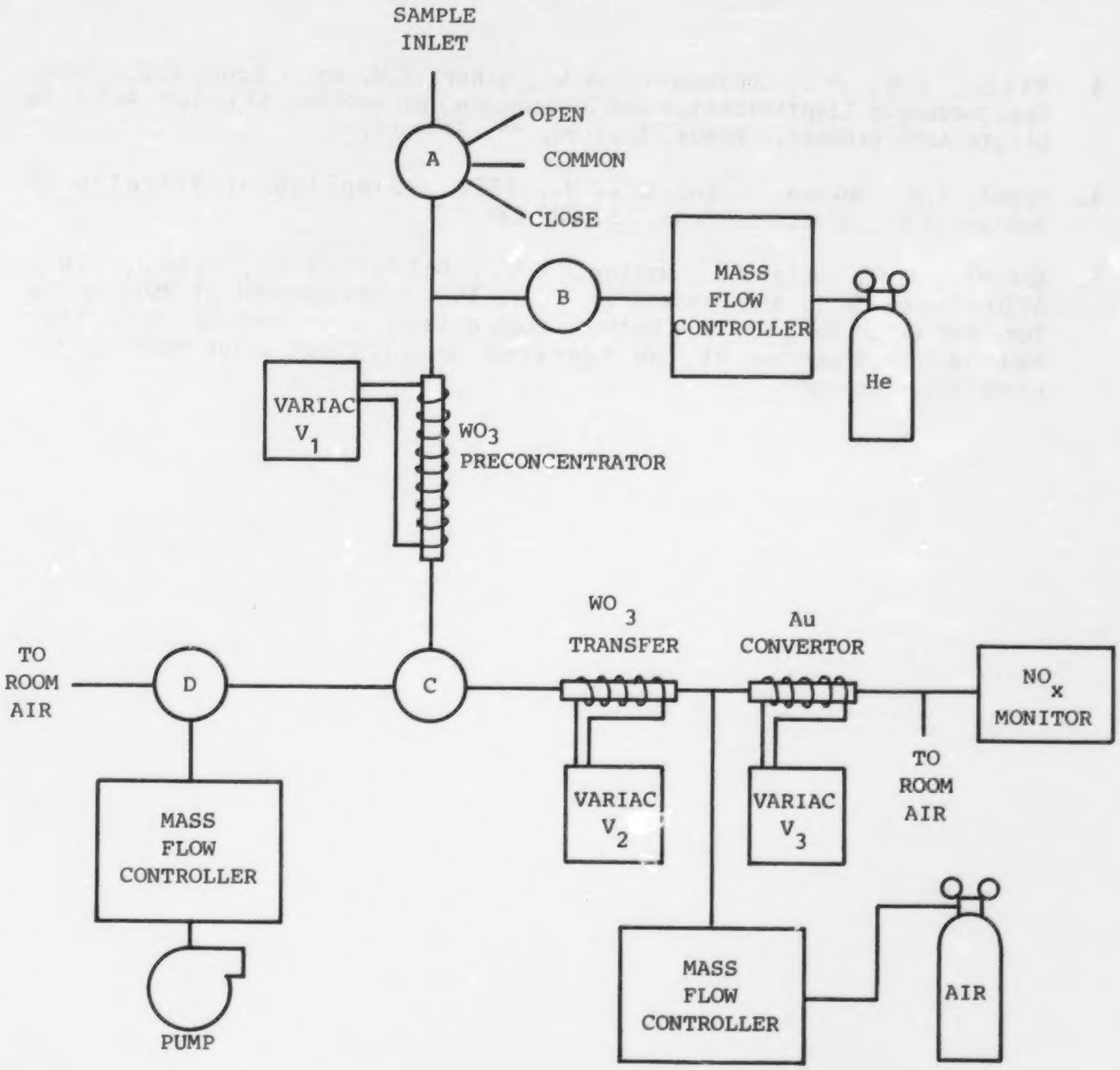
1. Braman, R.S., Shelley, T.J. and McClenny, W.A., 1982. Tungstic Acid for Preconcentration and Determination of Gaseous and Particulate Ammonia and Nitric Acid in Ambient Air. Anal. Chem. 54, 358-364.

2. Gailey, P.C., McClenny, W.A., Braman, R.S. and Shelley, T.J., 1983. A Simple Design for Automation of the Tungsten VI Oxide Technique for Measurement of NH_3 and HNO_3. Atmos. Environ. 17, 1517-1519.

3. Pitts, J.N. Jr., Biermann, H.W., Winer, A.M. and Tuazon, E.C., 1984. Spectroscopic Identification and Measurement of Gaseous Nitrous Acid in Dilute Auto Exhaust. Atmos. Environ. 18, 847-854.

4. Appel, B.R., Tokiwa, Y. and Haik. M., 1980. Sampling of Nitrates in Ambient Air. Atmos. Environ. 15, 283-289.

5. Roberts, J.M., Hubler, G., Norton, R.G., Goldan, P.D., Fahey, D.W., Albritton, D.L. and Fehsenfeld, F.C., 1984. Measurement of HNO_3 by the Tungsten Oxide Denuder Tube Method: Comparison with the Nylon Filter Method. Presented at the American Geophysical Union Meeting, San Francisco, December.


SAMPLE INLET
OPEN
A
COMMON
CLOSE
B
MASS FLOW CONTROLLER
He
VARIAC V_1
WO_3 PRECONCENTRATOR
TO ROOM AIR
D
C
WO_3 TRANSFER
Au CONVERTOR
NO_x MONITOR
TO ROOM AIR
VARIAC V_2
VARIAC V_3
MASS FLOW CONTROLLER
PUMP
MASS FLOW CONTROLLER
AIR

A = MOTOR-DRIVEN TEFLON BALL VALVE
B = NORMALLY CLOSED TWO-WAY SOLENOID VALVE
C = THREE-WAY TEFLON SOLENOID VALVES

Figure 1. Schematic of Automated Tungstic Acid Technique

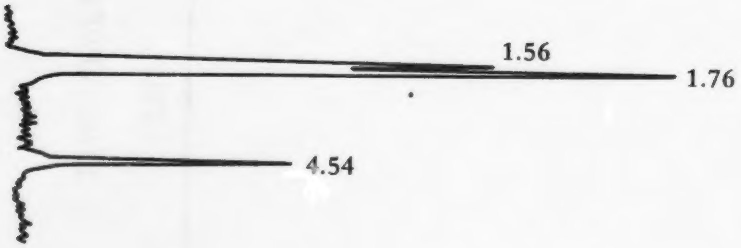


Figure 2. Possible Detection of Atmospheric Nitrous Acid Together With HNO_3 (0500 hr, 9/17/84)

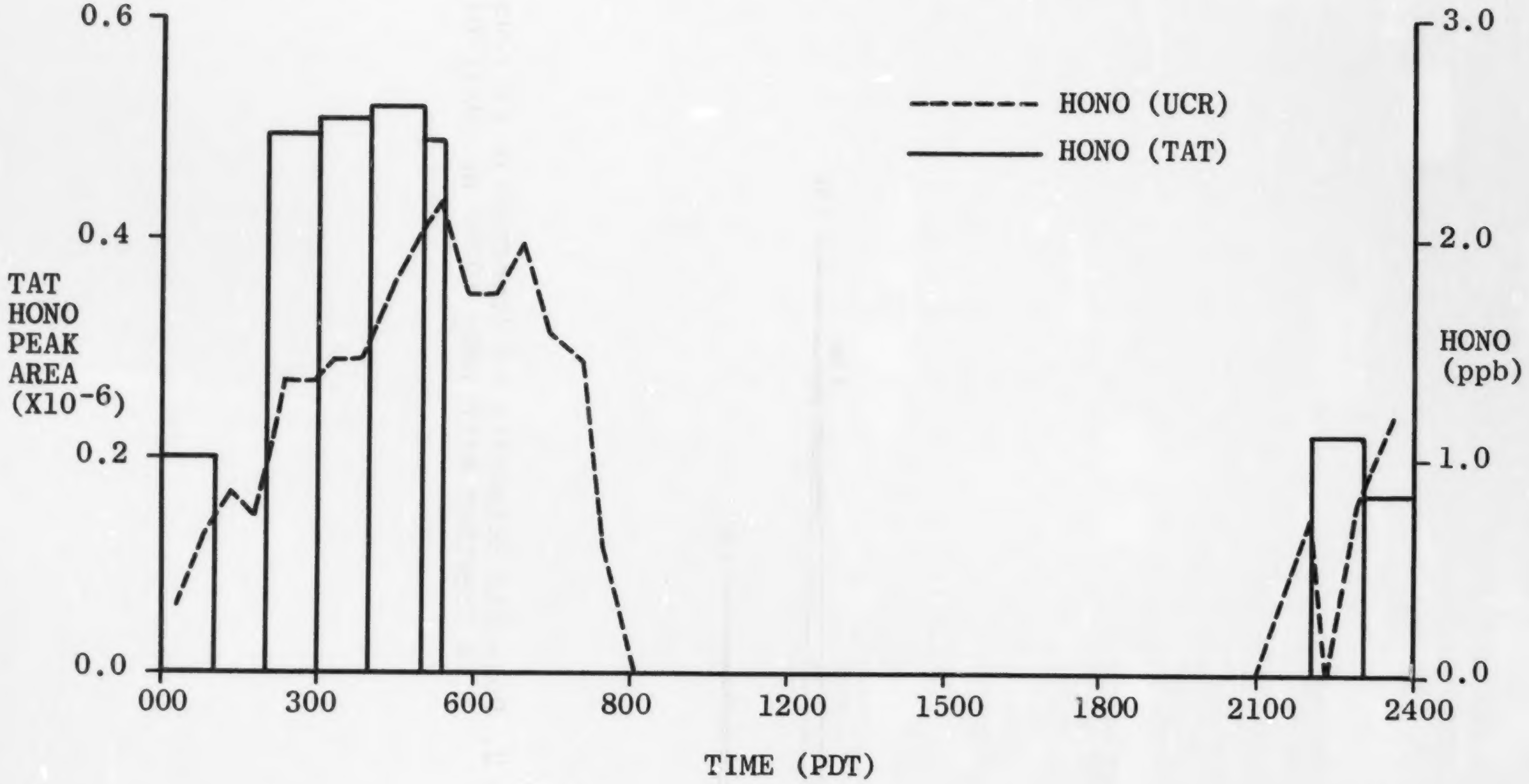


Figure 3. Comparison of UCR HONO Concentrations and TAT Peak Areas for HONO (9/18/84)

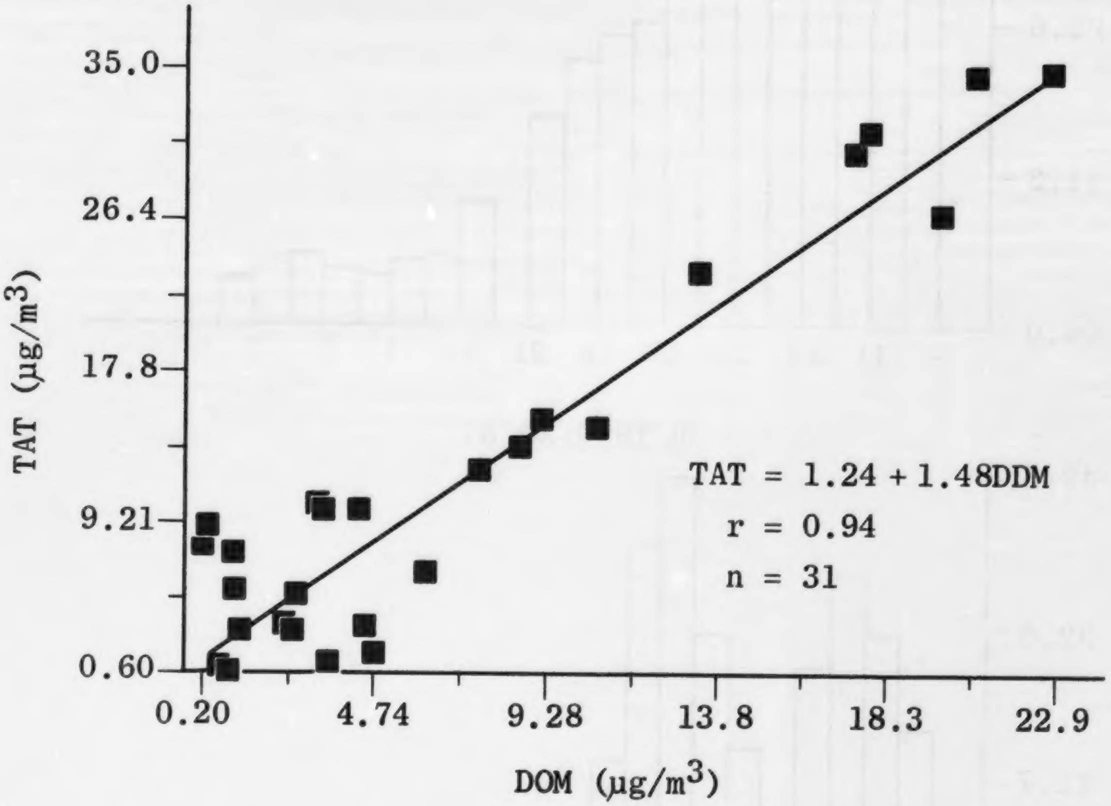


Figure 4. Comparison of Atmospheric HNO_3 Concentrations Measured by the Denuder Difference Method and Automated Tungstic Acid Technique

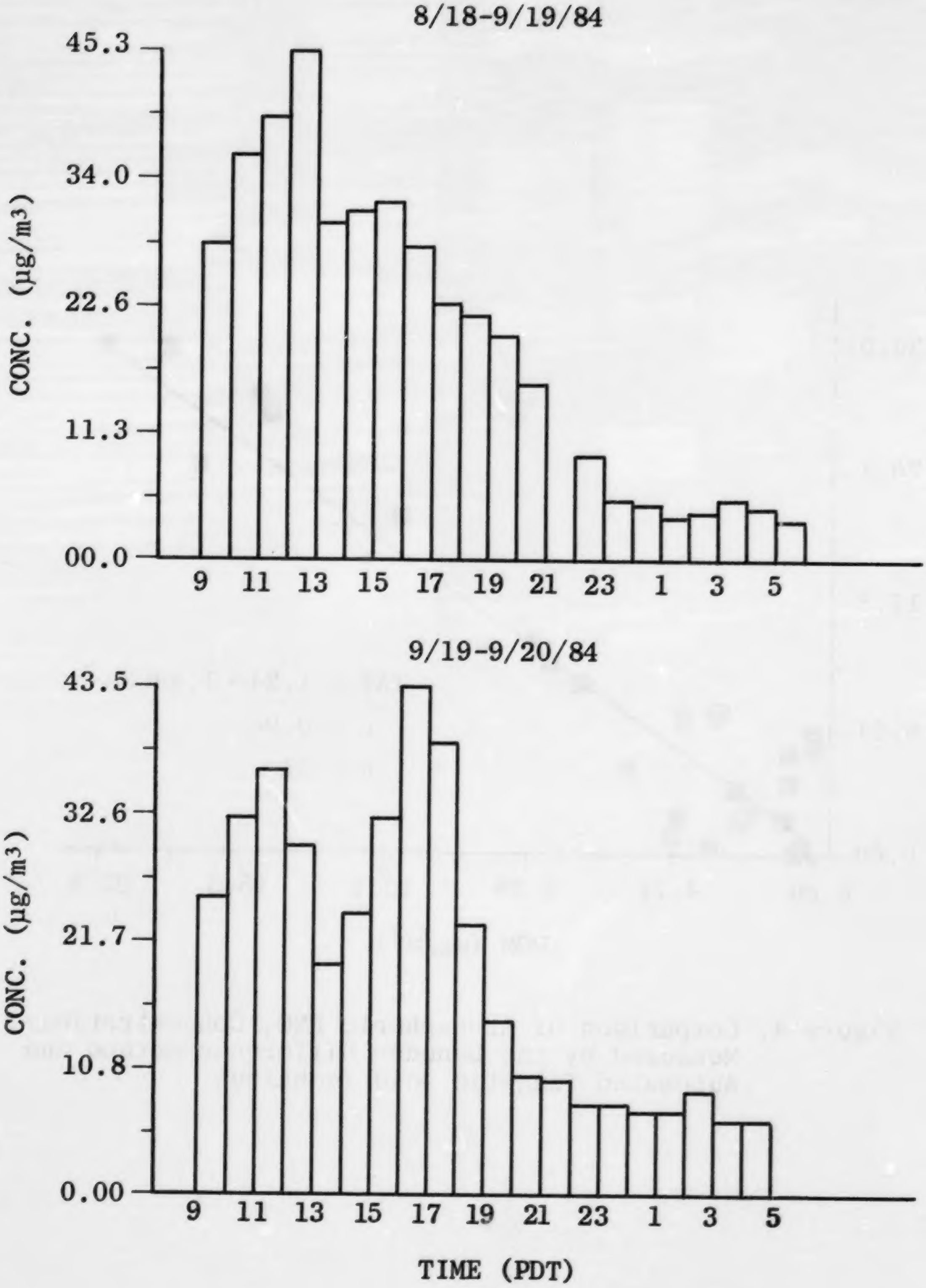


Figure 5. Diurnal Variation of HNO_3 at Riverside as Measured with the TAT

APPLICATION OF THE TUNGSTEN OXIDE DENUDER TUBE TECHNIQUE TO THE MEASUREMENT OF NITRIC ACID IN THE RURAL TROPOSPHERE AND COMPARISON WITH THE NYLON FILTER METHOD

J. M. Roberts*, R. B. Norton, P. D. Goldan, F. C. Fehsenfeld*,
and D. L. Albritton
Aeronomy Laboratory
National Oceanic and Atmospheric Administration
Boulder, CO 80303

*Also, Cooperative Institute for Research in the Environmental Sciences, NOAA, University of Colorado, Boulder, CO 80309.

Nitric acid (HNO_3) is an important species in rural atmospheres because it is a major end product of tropospheric odd-nitrogen (NO_y) chemistry, and because it is a major constituent of acid deposition. It is desirable to have a relatively fast measurement (15-30 min) of HNO_3 in the 10-100 pptv range for use in precipitation removal and dry deposition studies and for comparison with measurements of other NO_y species such as NO and NO_2 which can also be made on a short time scale. The tungsten oxide denuder tube technique, originally described by Braman et al. (1982), was applied to the measurement of HNO_3 in the rural troposphere. Laboratory studies of HNO_3 collection and recovery efficiency were performed along with tests for the interference of other trace nitrogen-containing compounds. Ambient measurements were made at a rural site in the Colorado mountains, and the results of those measurements compared to measurements of HNO_3 made by the more established Teflon/nylon filter pair method.

The basis of the tungsten oxide denuder tube technique is the selective chemisorption of $HNO_{3(g)}$ (and $NH_{3(g)}$) onto the inside surface of a tube coated with tungsten oxide. Nitrate and NH_4^+, present on aerosols, are not collected due to the greatly slower diffusion rates of aerosols relative to gas molecules. HNO_3 and NH_3 are removed from the tungsten oxide surface by thermal desorption. Nitric acid is desorbed from the surface as NO or NO_2, NH_3 is desorbed as NH_3. The compounds evolved from the surface are then converted to NO and analyzed by the well-known NO-O_3 chemiluminescence method. HNO_3 and NH_3 can be separated either by recollection of NH_3 or by temperature programmed desorption. Due to the preconcentration obtained by sampling through a coated tube and the inherent sensitivity of the chemiluminescent method, this technique can yield a short time scale measurement of HNO_3 at low concentrations.

Tungsten oxide coatings were prepared in a manner similar to that described by Braman et al. (1982). Modifications to this method involved progressive zone coating. In this technique, tungsten (IV) blue oxide was evolved from a short length (∿ 4 cm) of tungsten filament that was connected between 0.25 in. metal rods. This arrangement could be progressively moved along the length of the tube to produce a uniform coating of the tungsten oxide on the inside wall of the tube. The blue oxide so deposited on quartz tubing was then oxidized to the green-yellow oxide (WO_x) at approximately 350°C under clean air flow. This procedure was found to produce a more uniform coating than the single-filament technique of Braman et al. (1982).

Collection and recovery of HNO_3 and the extent of interference from other compounds were studied using the system shown in Figure 1. The system consisted of a commercial NO monitor with a carbon monoxide-doped gold catalyst operated at 725°C. The catalyst and NO monitor served to detect the compounds being examined. Connected to the detector was a 4-port valve which served to switch the WO_x tube in and out of line with the detector and the sample stream. The sample stream consisted of either dry or humidified zero-air with analyte species added. Collection efficiency of the WO_x tube was determined directly by switching the WO_x in-line with the detector and a sample stream containing a constant level of an analyte species. The resulting decrease in the detector signal was compared to the signal produced by the constant analyte level to obtain a % collection. After the desired collection time, the WO_x tube was switched out-of-line and the detector signal was observed to return to that representing the constant analyte level. Desorption of material from the WO_x tube was accomplished by switching the WO_x tube in-line with the detector and dry zero-air stream and heating the tube to 500°C. Heat was applied by a variable transformer connected to a Ni-Cr wire wound around the outside of the tube. Desorptions performed in this manner produced well defined peaks in the detector. The area under the peak could be compared to the area representing the amount of material collected to determine a % recovery. A flow rate of 700 sccm was used with a WO_x coating length of 40 cm. The collection and recovery of HNO_3 was observed to be 95±5% in dry (<2.6 ppm H_2O) air, and 100±3% for NH_3 under the same conditions. The collection and recovery of HNO_3 decreased slightly with the addition of water to the sample stream, possibly due to the clustering of HNO_3 with H_2O (Eatough, 1985).

Possible interferences of other nitrogen containing compounds were also tested at a range of H_2O concentrations with the system shown in Figure 1. The results of studies involving NO_2, n-propylnitrate, peroxyacetylnitrate (PAN), and hydrogen cyanide (HCN) are shown in Figure 2. The % response plotted on the vertical scale consists of the amount of material recovered during desorption divided by the total amount of material that the tungsten oxide tube was exposed to. In each case, it was apparent from the collection profile that incomplete collection was responsible for the reduced overall response to these compounds. Nitrogen dioxide is perhaps the most important potential interferant in the atmosphere, but was not collected in the WO_x tube to any significant extent (<1.5%). PAN was collected at 60% efficiency in dry air (<2.6 ppm H_2O) but at only 6% efficiency at 18% R.H. Additional ambient air tests confirmed that PAN was not an interferant. A representative alkyl nitrate, n-propylnitrate (NPN) was found to be collected with 55% efficiency in dry air, but at 90% R.H. the collection efficiency was only 0.2%. Although NPN was not checked at intermediate H_2O concentrations, based on the behavior of PAN it is unlikely that significant collection occurs at lower H_2O concentrations (i.e., 20% R.H.). Hydrogen cyanide was collected with only 10% efficiency in dry air, less than 3% efficiency for R.H. $\gtrsim$ 10%.

Ambient measurements of HNO_3 were made between July and November, 1984 using the tungsten oxide denuder tube method and the Teflon/nylon filter pair method. The measurement site was located approximately 35 miles northwest of the Denver/Boulder metropolitan area on Niwot Ridge, Colorado (10,000 ft. elev.). The prevailing winds bring in clean continental air masses to the site from the west. However, late morning to mid-afternoon warming of the eastern mountain slopes produces an upslope circulation bringing air from the front range urban corridor to the site.

The tungsten oxide ambient sampling system is shown schematically in Figure 3. The WO_x coated tube and gold catalyst were mounted on top of the instrument enclosure. The 6-port valve and all the gas lines were made of Teflon. The WO_x tube was made of quartz and had two 1/8" O.D. quartz lines teed into it for standards and zero-air desorption flow. The zero-air flow was set so that with the 6-port valve in the "analyze" position, there was a slight overflow out the inlet of the WO_x tube. The sample flow used was 1 slpm and sample time was 18 min. The desorption of HNO_3 and NH_3 was accomplished by a linear temperature program of the WO_x section from ambient to 525°C. A resulting desorption profile is shown in Figure 4. Standards were obtained from permeation tubes which were calibrated by conversion to NO in the gold catalyst and analyzed by NO-O_3 chemiluminescence. Standards were introduced to the WO_x tube, either in an excess of zero-air (dry or humidified) or in a small flow (50 sccm). The detection limit was approximately 30 pptv HNO_3 and the overall uncertainty ±20% at HNO_3 mixing ratios of 100 pptv or more.

The Teflon/nylon filter pair method has been widely applied to the measurement of HNO_3 in the rural troposphere. Details of our tests of this method can be found in Goldan et al., 1983. These tests show that there was negligible collection of $HNO_{3(g)}$ on the Teflon aerosol filter and >90% collection of HNO_3 on the downstream nylon filter. Additional tests using side-by-side sets of filter pairs showed that volatilization of NO_3^- (as NH_4NO_3 or HNO_3) from the Teflon filter onto the nylon filter was, at most, a 10% positive interference in the HNO_3 measurement. Since the collected NO_3^- is analyzed by ion chromatography, a relatively insensitive technique, large volumes of air must be sampled over several hours with this technique.

Results of simultaneous measurements of HNO_3 by the WO_x tube technique HNO_3 (WO_x) and the nylon filter method are shown in Figure 5. The tungsten oxide measurements are averages of measurements made during the 2- or 4-hour nylon filter sample time. The results show that the tungsten oxide method measured, on the average, 3 times more "apparent" HNO_3 than the nylon filter method. The discrepancy between the two methods is sometimes as much as a factor of ten. Only two points are at or below the 1:1 tungsten oxide-nylon line. Thus, it appears that other species are collected on the WO_x surface and interfere with the HNO_3 measurement.

A dual tube system was employed to check for the presence of interfering compounds. The two tubes run side-by-side agreed to within 15%. Nylon wool was placed in the inlet of one tube to remove HNO_3. The tube with the nylon wool trap gave three measurements of 270±60 pptv (average) while the untrapped tube gave three measurements of 500 pptv. The difference, 230 pptv, compared very well with the nylon filter measurement of 190 pptv made just subsequent to the WO_x tube measurements. Therefore, we conclude that there are other nitrogen containing species that are collected on the WO_x surface and interfere with HNO_3.

Possible synergistic collection of PAN from a whole air sample was tested by the addition of a small stream (50 sccm) containing PAN to every-other ambient sample collected in the WO_x tube. The equivalent mixing ratio of PAN at the 1 slpm sample flow was 1100 to 890 pptv. No significant difference was noted in the ambient measurements with and without added PAN, which confirmed that PAN is collected at <5% efficiency under ambient conditions.

Correlations of HNO_3 (WO_x) with other odd-nitrogen species measured at this site were examined for clues as to the identity of the interfering species. The correlation of HNO_3 (WO_x) with NO_x ($NO + NO_2$) (Singh et al., 1985) showed that the interfering species are probably photochemical products of NO_x. The correlation of HNO_3 (WO_x) with PAN (Singh et al., 1985) was very good, indicating that the interfering species, although not PAN, may be PAN-type compounds, i.e. organic nitrates. This seems to be a feasible explanation, since a wide variety of organic nitrates are thought to result from organic photochemistry (Atkinson et al., 1982) or nitrate radical (NO_3) chemistry (Bandow et al., 1980).

ACKNOWLEDGEMENTS

We thank the staff of the University of Colorado Institute for Arctic and Alpine Research for their logistical support at the Niwot Ridge site. This work was supported by the National Oceanic and Atmospheric Administration as part of the National Acid Precipitation Assessment Program.

REFERENCES

Atkinson, R., S.M. Aschmann, W.P.L. Carter, A.M. Winer, J.N. Pitts, Jr., (1982), Alkyl nitrate formation from the NO_x-air photooxidation of C_2-C_8 alkanes, J. Phys. Chem., 86, 4563-4569.

Bandow, H., M. Okuda, H. Akimoto, (1980), Mechanism of the gas-phase reaction of C_3H_6 and NO_3 radicals, J. Phys. Chem., 84, 3604-3608.

Braman, R.S., T.J. Shelley, W.A. McClenny, (1982), Tungstic acid for preconcentration and determination of gaseous and particulate ammonia and nitric acid in ambient air, Anal. Chem., 54, 358-364.

Eatough, D.J., V.F. White, L.D. Hansen, N.L. Eatough, E.C. Ellis, (1985), Hydration of nitric acid and its collection in the atmosphere by diffusion denuders, Anal. Chem., 57, 743-748.

Singh, H.B., L.J. Salas, B.A. Ridley, J. Shetter, F.C. Fehsenfeld, D.W. Fahey, D.D. Parrish, E.J. Williams, S.C. Liu, (1985), Relationship between peroxyacetyl nitrate (PAN) and nitrogen oxides in the clean troposphere. Submitted to Nature.

FIGURE CAPTIONS

Figure 1.	Laboratory system used for collection/desorption and interference studies.
Figure 2.	Results of interference tests involving NO_2, HCN, n-propylnitrate, and PAN.
Figure 3.	Tungsten oxide denuder tube system used for ambient air measurements.
Figure 4.	Desorption profile of an ambient air sample.
Figure 5.	Nitric acid measured by the tungsten oxide tube, $HNO_3(WO_x)$, vs. HNO_3 measured by the Teflon/nylon filter pair.

Figure 1.

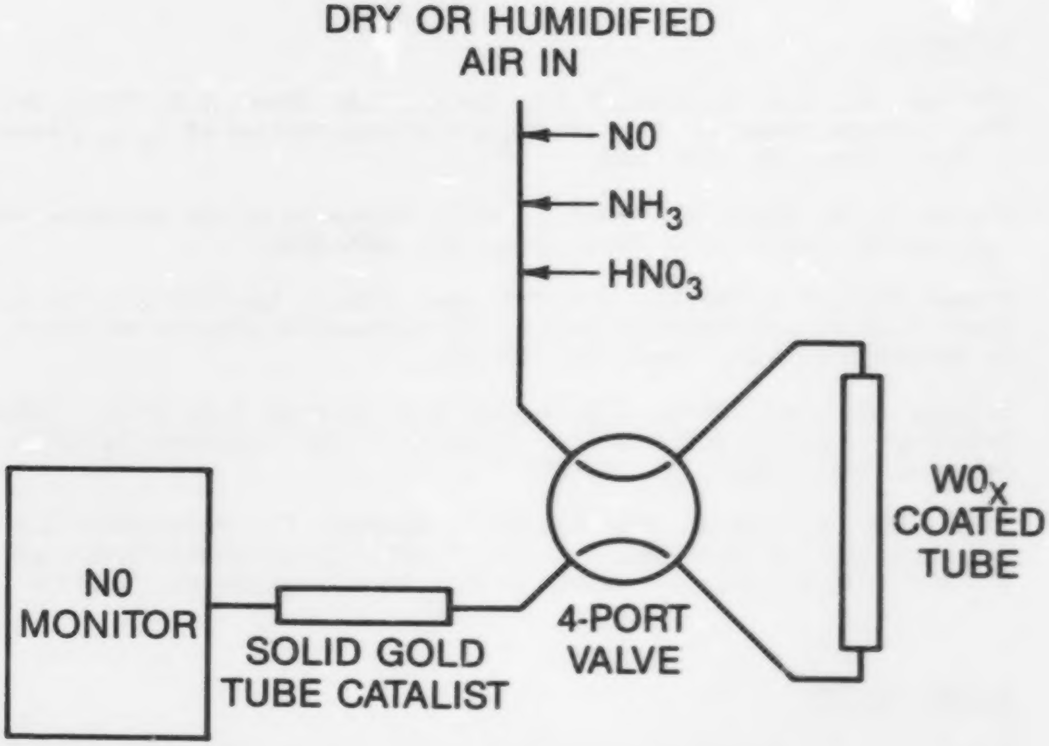

DRY OR HUMIDIFIED AIR IN
N0
NH_3
$HN0_3$
$W0_X$ COATED TUBE
N0 MONITOR
SOLID GOLD TUBE CATALIST
4-PORT VALVE

Figure 2.

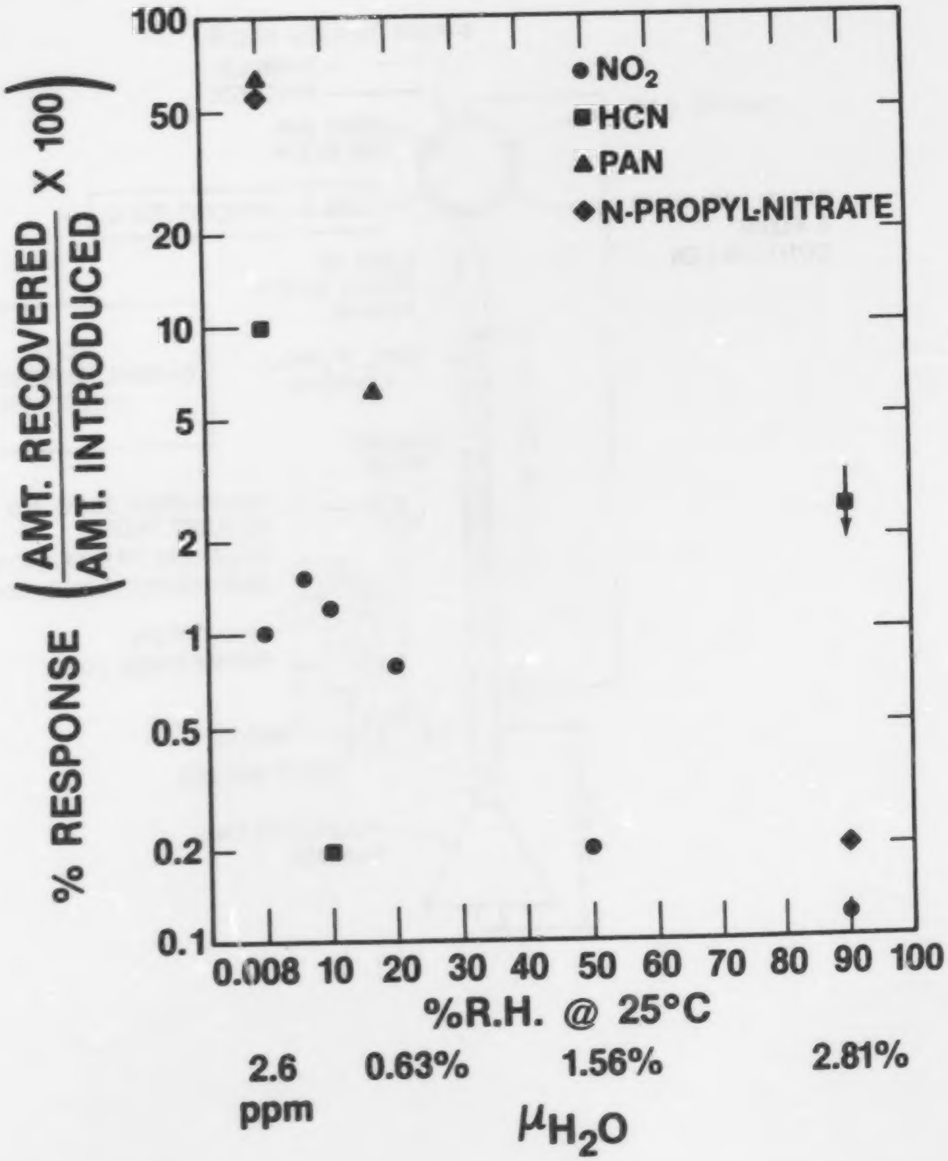
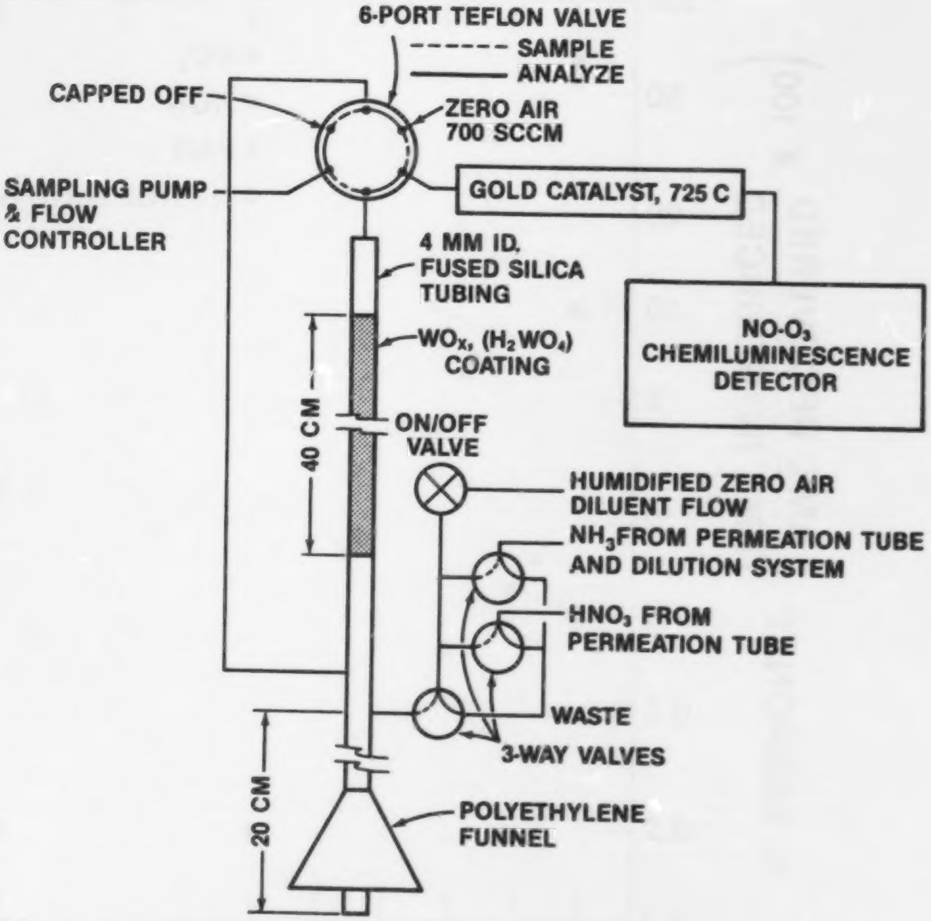
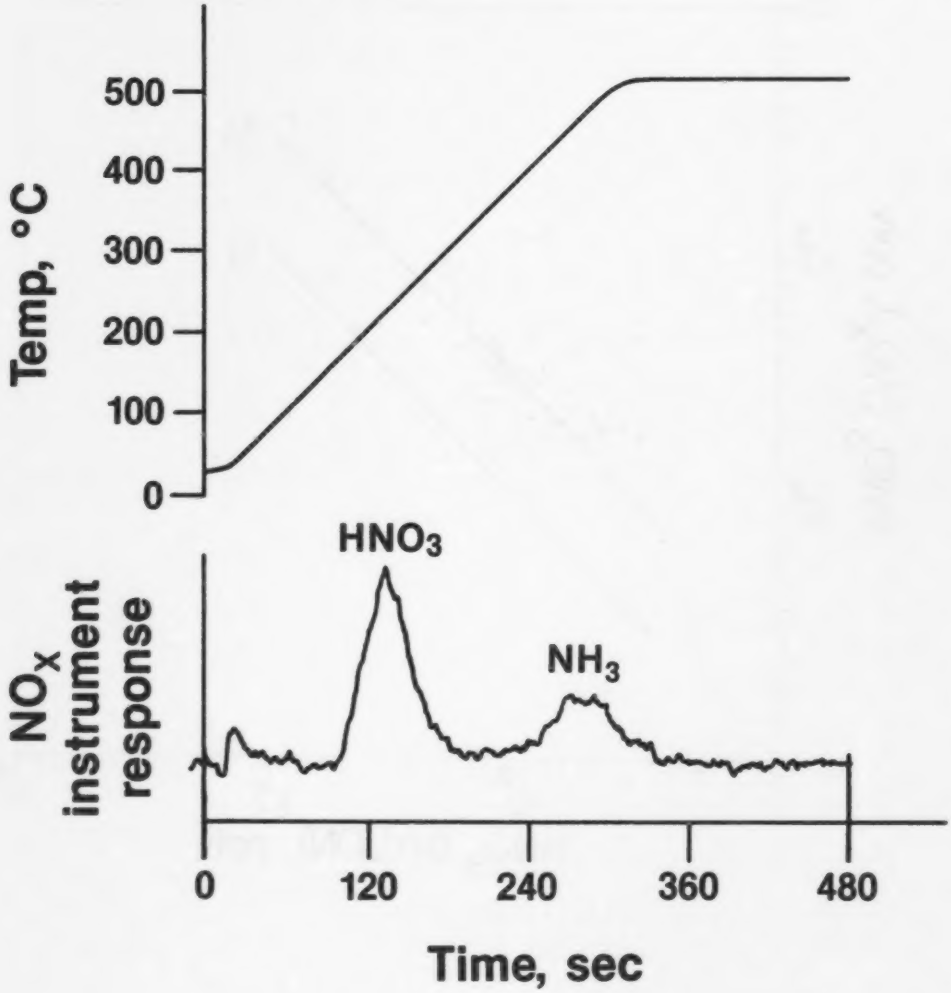

% RESPONSE $\left(\frac{\text{AMT. RECOVERED}}{\text{AMT. INTRODUCED}} \times 100\right)$
100
50
20
10
5
2
1
0.5
0.2
0.1
● NO_2
■ HCN
▲ PAN
◆ N-PROPYL-NITRATE
0.008
10
20
30
40
50
60
70
80
90
100
%R.H. @ 25°C
2.6 ppm
0.63%
1.56%
2.81%
μ_{H_2O}

Figure 3.



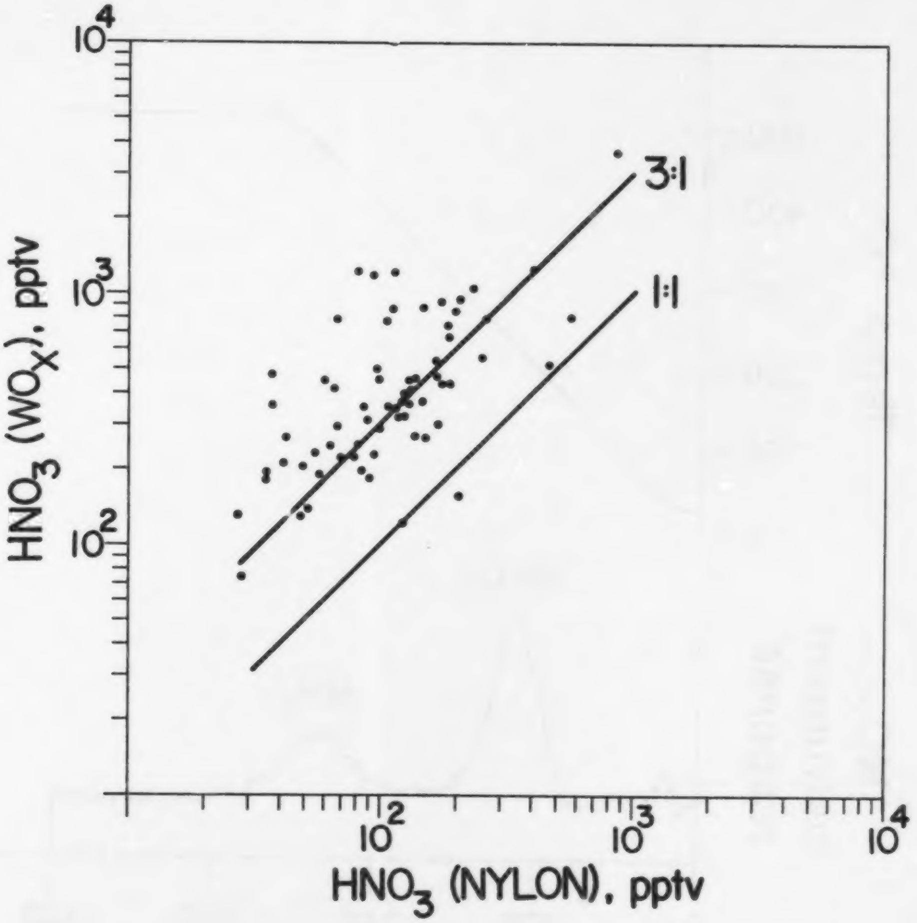
6-PORT TEFLON VALVE
------ SAMPLE
—— ANALYZE
CAPPED OFF
ZERO AIR 700 SCCM
SAMPLING PUMP & FLOW CONTROLLER
GOLD CATALYST, 725 C
4 MM ID. FUSED SILICA TUBING
WO_x, (H_2WO_4) COATING
NO-O_3 CHEMILUMINESCENCE DETECTOR
40 CM
ON/OFF VALVE
HUMIDIFIED ZERO AIR DILUENT FLOW
NH_3 FROM PERMEATION TUBE AND DILUTION SYSTEM
HNO_3 FROM PERMEATION TUBE
WASTE
3-WAY VALVES
20 CM
POLYETHYLENE FUNNEL

Figure 4.



Temp, °C
500
400
300
200
100
0
HNO_3
NH_3
NO_X instrument response
0
120
240
360
480
Time, sec

Figure 5.



THE USE OF LICHENS TO MEASURE THE TRANSPORT OF AIRBORNE HEAVY METAL POLLUTANTS

James N. Beck, Robert L. Thompson, Celinda Mueller, Dennis Casserly,
Pam Langley and John Young
Department of Chemistry
McNeese State University

INTRODUCTION Lichens have been known to be sensitive to air pollutants since 1859 when it was observed that lichens were disappearing from Manchester England. A variety of heavy metals are associated with air pollutants from such industries as power generators, refineries, smelters, etc. Lichens absorb heavy metals primarily from dissolved ions in rain water and retain them for long periods of time. It was thus felt that the Lake Charles, LA, area was an ideal area to observe long range changes in concentrations of heavy metals since the industrial complex is centrally and locally concentrated in the parish. This study area is also isloated from other heavily industrialized centers. The plants include two oil refineries, coal-fired power plant, four chemical plants and an aluminum plant. Lichens were collected from 16 stations located in a grid around the industrial corridor in Calcasieu Parish located in extreme southwest Louisiana. In addition, two stations were also established in Cameron Parish lying south of Calcasieu Parish and bordering on the Gulf of Mexico. These two stations were selected to serve as control stations. The collections were done during three seasons in 1983-1984 to determine if variations with distance and time occur across the Parish, and the magnitude of the variations.

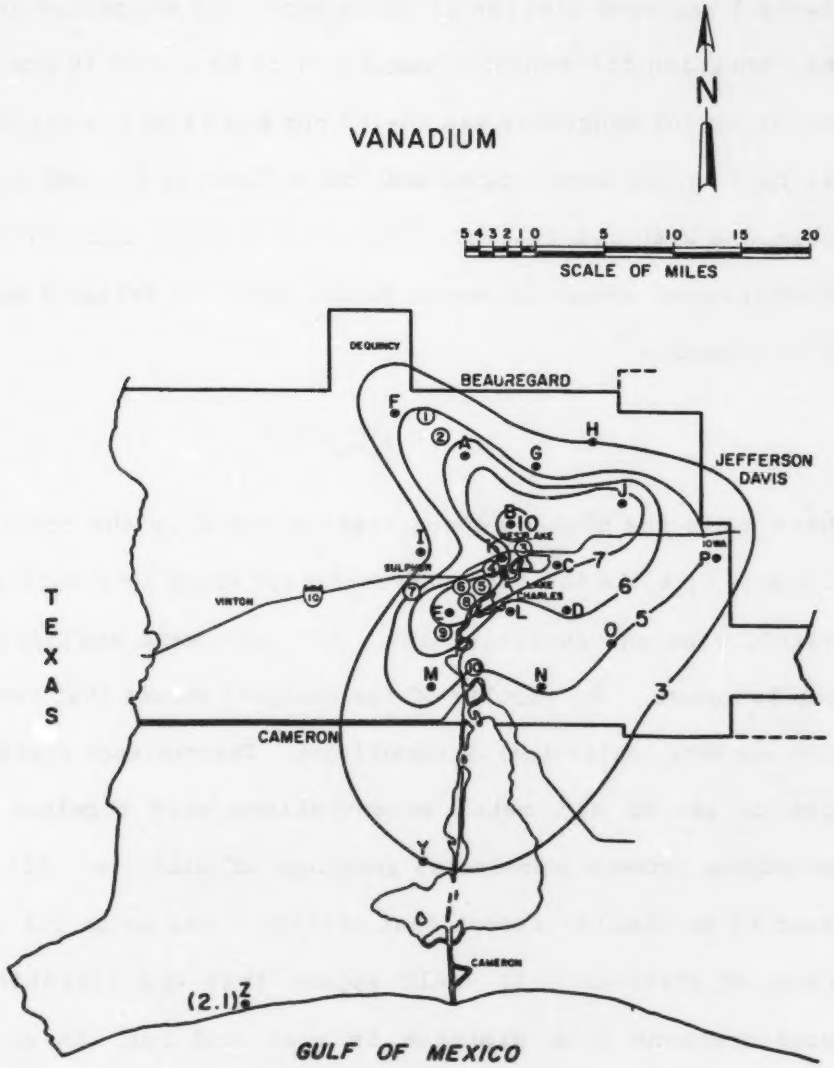
EXPERIMENTAL The lichens Parmelia praesorediosa and Ramalina stenospora were collected using teflon coated tweezers from the trunk and lower branches of oak trees. The lichens were placed in preweighed plastic irradiation vials and labeled by station, date and lichen type by code number on the vial. Collections were done on three occasions, August 1983, February and May 1984. This was done to observe seasonal differences in metal uptake or elimination. The May sampling survey followed an extended period of dry weather. The samples were then irradiated for fifteen seconds at the Texas A&M University 1 MW pool reactor at a flux of 10^{13} n cm^{-2} sec^{-1}. The samples were counted after a fixed delay time on a Harshaw Ge(Li) detector and the spectra stored and analyzed using a Hewlett Packard Scorpio multichannel analyzer. This method allowed the determination of vanadium, aluminum, manganese and in a few lichens calcium, titanium and copper.

RESULTS AND DISCUSION An example of the results of the analysis of the data are given in Figure 1 for vanadium. The stations are given by letters and the industries are given as circled numbers. Ths isolines were drawn through stations having concentrations equal to the value of the isoline. It is clear that the highest values of vanadium are located, as expected, near the industrial corridor in central Calcasieu Parish. The lower values were found along the Gulf of Mexico more than 80 km from the industries. However, it is clear that the concentrations decrease regularly from the industrial corridor. The only exception from this trend was toward the northwest where the decrease is more rapid. However, few stations are located in that direction and this may have affected the results. The data plotted are the means for all lichens and the three sampling periods. The trend shown for vanadium in Figure 1 was very similar to those shown for manganese and aluminum. The variation for vanadium was found to be 2.1 to 10 ppm whereas the variation for manganese was 20-180 ppm and aluminum was 900-4500 ppm. All high values were located near the refineries located near West Lake, Louisiana with all low values located near the Gulf of Mexico. The concentrations across Calcasieu Parish appear to follow a decrease given by an equation:

$$C = C_o e^{-\lambda_\tau D}$$

where C_o is the highest concentration and C is the concentration at distance D, λ_τ is the disappearance rate which is a function of stack height, wind and particle size. All data were analyzed using SPSS computer codes. The results of the analysis showed that variations with distance were statistically significant. Discriminant analysis was also done to see if all metal conentrations used together would show variations between preselected groupings of stations. All groups were found to be similar except that station I had to be put in the outer group of stations. It would appear that the variation of metal concentrations with distance is real and has its origin in the industrial corridor.

Figure 1. The variation of the concentrations of vanadium (ppm) across Calcasieu Parish, Louisiana. The sampling stations are given as letters and the major industries as circled numbers. The lines drawn connect stations having similar concentrations.


VANADIUM
N
5 4 3 2 1 0 5 10 15 20
SCALE OF MILES
DEQUINCY
BEAUREGARD
JEFFERSON DAVIS
TEXAS
CAMERON
VINTON
10
SULPHUR
WESTLAKE
LAKE CHARLES
IOWA
CAMERON
F
①
②
A
G
H
J
B
10
I
K
③
④
C
7
6
5
3
⑦
⑥
⑤
⑧
E
⑨
L
D
O
P
M
⑩
N
Y
(2.1) Z
GULF OF MEXICO

Measurement of HNO_3, SO_2, NH_3 and Particulate Nitrate with an Annular Denuder System

by

R. K. Stevens and R. J. Paur, U. S. Environmental Protection Agency
Research Triangle Park, NC

I. Allegrini, F. DeSantis, A. Febo, C. Perrino and M. Possanzini
CNR - Istituto Inquinamento Atmosferico, Rome, Italy

K. W. Cox, E. E. Estes, A. R. Turner and J. E. Sickles, II
Research Triangle Institute, Research Triangle Park, NC

Abstract

A ten-day study was carried out in the spring of 1985 in the Research Triangle Park to demonstrate the performance of a system based on the annular denuder method (ADM) for collection of a number of species of importance in acidic dry deposition. The ADM was compared with a denuder difference measurement (DDM) and filter pack for the measurement of gaseous nitric acid and particulate nitrate. The ADM sulfur dioxide collection and analysis precision was determined to be ±5% for sulfur dioxide concentrations in the range of 1 to 6 $\mu g/m^3$; the precision for HNO_3 was ±4% over the concentration range of 0.2 to 1.6 $\mu g/m^3$. The sensitivity of the ADM is approximately 0.6 μg for eitther NO_3^- and $SO_4^=$, corresponding to a nitric acid or SO_2 concentration of approximately 0.1 $\mu g/m^3$ sampled at 15 liters/min over a 6 hour interval.

Preliminary results from the comparison of nitric acid measurements indicate that the ADM and the DDM give the same results to ±20% at concentrations of 1 $\mu g/m^3$ and 12 hour sample intervals. Details of the experimental protocol and results are discussed in this paper.

Introduction

A number of primary and secondary air pollutants contribute to the acidity in depositions from the atmosphere onto receptors such as soils, vegetation, bodies of water and man-made surfaces. The gaseous and particulate pollutant species that are postulated to be among the major contributors to acidic deposition are listed in Table 1. Typical non-urban concentrations of those species are also presented in the table.

Commercial instrumental methods are available to monitor some of these pollutants, such as SO_2, NO, NO_2 and O_3. However, the sensitivity of these instruments is not adequate to measure these pollutants, except for O_3, at the concentrations typically found in non-urban locations. In addition, the cost and maintenance of these monitors is often prohibitive for many air quality studies. For these reasons a number of investigators over the past five years have been developing filter packs and denuders to measure these species by conventional wet chemical procedures.

During the past two years a new denuder design -- the annular denuder -- has been developed and tested at the Laboratory for Atmospheric Pollution of C.N.R., Rome, (Italy) which has led to a device described by Possanzini et al. (1983) that is suitable for the simultaneous measurement of gaseous and particulate species, such as HNO_3, NO_3^-, HNO_2, NH_3, SO_2, and $SO_4^=$, which contribute to deposition. The U.S. Environmental Protection Agency (US EPA) invited a team from C.N.R., Rome, Italy to bring the equipment needed for the measurement of acid species and to compare the results with those obtained with devices currently being evaluated by the Research Triangle Institute in North Carolina for the US EPA. The principles and characteristics of the annular denuder method (ADM) and the results from the field study are described below.

The objective of the field study was to compare an annular denuder system with the widely used denuder difference method (DDM) of Shaw et al. (1982) to determine whether there are advantages over the conventional DDM system to warrant additional research on annular denuders in the EPA methods development program. This brief study relied on (a) a comparison of the performance of open-tube and annular denuders, coupled with filter packs, to measure ambient concentration of HNO_3, SO_2 and particulate nitrates, and (2) a determination of the precision of the annular denuder method for the measurement of SO_2 and HNO_3 to estimate the value of a more detailed evaluation/development program for the annular denuders.

Principles and Characteristics of the Annular Denuder System

The C.N.R. denuder is an annular tube configuration (Fig. 1). During sampling, air is drawn under laminar flow conditions through the annular space between two concentric glass cylinders that have been coated with a chemical that reacts with selected trace species. As the sample stream passes through the annular space, the gaseous trace species travel by molecular diffusion from the bulk gas to the reactive surface and are collected.

The reader is referred to the work of Pozzanini, et al. (1983) for a discussion of annular denuder tube theory. The operational summary of the theoretical comparison of the denuders described in Table 2 is:

$$\frac{F}{L_a} = 30 \frac{F}{L_T}$$

where

F is the flow rate
L_a = length of annular denuder
L_T = length of open tube denuder

For a given flow the annular denuder can achieve equivalent collection efficiency in ~1/30 of the length required for an open-tube denuder, or for a given denuder length, the annular denuder can sample at ~ 30 times the flow of an open-tube denuder.

The high operating flow rate (10-30 ℓmin^{-1}) makes the annular denuder very useful for experiments where collection of low concentration of certain gases are required over short term sampling (1-4 h) periods. The high flow rate also permits more material to be collected on membrane filters downstream of the denuder. Previously, collection of large quantities of particles while simultaneously preserving the integrity of the particles through removal of reactive gases (eg, HNO_3, NH_3, and SO_2) required that the filter be preceded by a parallel multitube denuder assembly similar to that described by Stevens, et al (1979).

For a denuder to be effective, the system needs to ensure separation of the gases and particles. However, diffusional and inertial deposition at the inlet can result in particle uptake which has been determined experimentally (Possanzini et al., 1983) to be not larger than about 3%. The transit time of air through the denuder is <0.1 second, reducing the opportunity for substantial disturbance of the atmospheric gas-particle equilibrium existing in the atmosphere. The walls of the denuder are etched by sand blasting with 100 μm sand particles. This feature increases the surface area available for chemical coating and as a result the capacity of the denuder to collect the pollutants of interest can be increased to several milligrams.

The use of a water soluble and IC compatible substrate to coat the walls of the tube (e.g., Na_2CO_3) simplifies the extraction and the analysis of the sample. Other substances deposited on the denuder may give rise to the formation of the same ions; for example, deposition of particulate matter containing chlorides, sulfates and nitrates interfere with the measurement of HCl, SO_2 and HNO_3. The absorption of NO_2 and PAN on Na_2CO_3 yield nitrites which interfere with the measurement of HNO_2. However, the efficiency for the collection of these interfering species is relatively small (about 1 to 3%) (Ferm and Sjödin, 1985, and Peak and Stevens, 1985). Thus, the amount of relatively unreactive interferents collected in the first denuder will be approximately equal to that found in the second denuder. This feature can be used to correct data obtained from the analysis of the first denuder. The use of two denuders in series will then permit the simultaneous analysis of several acidic compounds, even though the ratio of analytes in the gas phase and particulate matter is extremely low. For instance, the technique is valuable for the measurement of trace levels ($< 0.1\ \mu g/m^3$) of SO_2 and HNO_3 in the presence of large quantities of sulfates and nitrates in particulate matter and, in addition, the use of two denuders will permit the measurement of small amounts of HNO_2. The ADM permits short and long samplings (1 hr to 1 week), and permits determination of diurnal profile of the concentration of reactive species.

The Experiment

Experiments were conducted between March 27 and April 3, 1985. Samples were collected at the Research Triangle Institute's acid deposition research site located in the RTP, NC. The system based on the ADM is shown in Figure 2 and the DDM (Shaw et al 1982) is shown schematically in Figure 3. Table 2 summarizes the characteristics and operational conditions of the two types of denuder systems that were used during the field intercomparisons. Replicate 24 h, 12 h and 4 h ADM samples were collected; DDM samples were collected for 24 h and 12 h periods.

Annular Denuder: The flow rate through the ADM (Fig. 2) was maintained with downstream differential flow controllers. The ADM consisted of the following components:

(a) A cyclone for size segregation of particles entering the sampling train. In the present configuration a Teflon cyclone having a cut size of approximately 2.5 μm at 15 ℓ/min was used.

(b) Two annular denuders in series coated with a 1% Na_2CO_3 and 1% glycerine in a 1:1 water-methanol solution for the collection of acid species.

(c) A filter pack which accommodates a Teflon filter for the collection of particulate matter and a backup nylon filter to collect nitrates evaporated from the Teflon filter.

The components of the ADM are easily assembled by means of threaded rings and connectors. After sampling, the tubes can be recapped for safe transportation to the laboratories where analyses will be carried out.

Denuder Difference Method (DDM) Sampler: The sampler based on the DDM and used in this study (shown in Fig. 3) consists of the following components:

(a) Teflon cyclone to remove particles larger than 2.5 μm when operated at 28 ℓ/min.
(b) Teflon manifold located downstream of the cyclone.
(c) A tubular denuder coated with MgO followed by a 25 mm diameter nylon filter, 2 ℓ/min flows through this leg of the system
(d) A Teflon tube followed by a 25 mm diameter nylon filter, 2 ℓ/min flows through this leg of the system.
(e) Two Teflon filter packs containing a 47 mm diameter Teflon filter followed by a TEA-treated filter also collect aerosol from the main sampling manifold.

One 12-hour experiment was carried out to compare the collection efficiency of oxalic acid, phosphoric acid, and citric acid based denuder coatings for the collection of ammonia. A 1% solution of each acid in 1:99 glycerin/methanol solvent (20 ml total volume) was poured into separate denuders, the denuder was rotated to ensure complete coating of the surface, the excess solution was drained out and the denuder was dried with a clean air stream. The Na_2CO_3 coated tubes used for acidic species were prepared in a similar fashion.

Analysis: The nylon filters were extracted by adding 20 ml of Na_2CO_3 ion exchange solution to a 30 ml Nalgene bottle containing the filters. The extract is sonicated for 30 minutes and a aliquot injected into the ion chromotograph (IC) instrument for nitrate determination.

The annular denuders were extracted with 20 ml distilled water and aliquots analyzed by ion chromatography, or by colorimetry (Indophenol Blue Method) when ammonia was measured.

The IC analysis of the extract of the Na_2CO_3 denuders gives the concentration of chlorides, nitrites, nitrates and sulfates formed on the denuder by uptake of HCl, HNO_2, HNO_3 and SO_2, respectively.

Results and Discussion

Table 3 shows the results of replicate comparisons between two annular denuder assemblies. Also during these replicate comparisons, a DDM system collected samples during the 12 h and 24 h intervals in parallel with the ADM assemblies. The nylon filters from the DDM were extracted to determine the nitrate and nitric acid concentrations. The ambient nitrate concentration was typically less than 0.2 μg/m³; the DDM system was unable to make this measurement, since the flow rate through the open-tube denuders was only 2 ℓ/min and the amount of sample collected was too small for accurate determination. At these flow rates, for experiments lasting 12 hours, only 1.34 m³ of air is collected. If the concentration of nitrate is 0.2 μg/m³, then in a 20 ml extract the concentration of nitrate per ml is less than 0.01 μg/ml which is below the detection limit of the IC. Table 4 shows the HNO_3 data from ADM and DDM systems. We report only data for sampling periods > 12 hrs and when the concentrations of HNO_3 were near or greater than 1 μg/m³. These criteria for data selection are based on the limitation of the DDM noted above.

One experiment was performed to test the collection efficiency of three different acid coatings to collect NH_3. The coatings were phosphoric acid oxalic acid and citric acid. All three denuders collected, over a 16 hour sampling period April 4-5, 1985, 1.5 μg NH_3. The differences between the 3 collection devices were nominal. Since the citric acid is essentially non-volatile and compatible with both IC and colorimetric analysis, it is preferred as the denuder coating to collect NH_3. Ferm (1979) used oxalic acid coated denuders in his studies to collect NH_3. However, the volatility of oxalic acid makes its use questionable during hot summertime conditions.

The replicate SO_2 and HNO_3 data shown in Table 3 demonstrate that the reproducibility of the collection and analysis procedures used in this study were typically better than ± 5% for SO_2 over a concentration range of 1-6 μg/m^3 and ±4% for HNO_3 over a concentration range of 0.15-1.6 μg/m^3.

Figure 4 shows the concentrations of HNO_3 and particulate nitrate collected in 12 hr 'day-night' intervals. The results are consistent with photochemical theory predictions that HNO_3 concentrations would be higher during daylight hours and tend to diminish at night. The particulate nitrate data did not show a distinctive diurnal pattern.

An interesting feature of the annular denuder assembly used in this study was the HNO_2 data obtained from the extract of the Na_2CO_3 coated denuders. The HNO_2 concentrations were often greater than 0.2 μg/m^3 and, as predicted from photochemical principles, higher at night than during the daytime. Sjödin and Ferm (1985) have made this same general observation in studies performed in Götenburg, Sweden; however, for two months of their 5 month study they measured daytime HNO_2 levels greater than the nighttime levels. Recent annular denuder measurements reported by Peake and Stevens (1985) in Calgary, Alberta also observed high daytime (<0.5 μg/m^3) HNO_2 concentrations.

Fig. 5 shows an example of monitoring HNO_2 and HNO_3 at 3 hr sampling intervals in Rome, Italy in February 1985 with the same denuder assembly tested in the study described in this report. Nitric acid accumulates during the day and, due to its large deposition velocity, almost disappears overnight. Nitrous acid (HNO_2) concentration is typically higher at night because during the day it is rapidly photolized by the sunlight.

A typical chromatogram obtained from IC analysis of annular denuder extracts is shown in Fig. 6. There is no visual evidence of $SO_4^=$ or NO_3^- in the second denuder; this shows the high collection efficiency of the first denuder for HNO_3 and SO_2 and implies that deposition of particles in the denuder is low. Absence of NO_2^- in the second denuder is interpreted as an indication that the NO_2^- in the first denuder is due to a very reactive species such as HNO_2 rather than PAN or NO_2, which react much more slowly with the Na_2CO_3 denuder surface (Ferm and Sjödin, 1985).

Summary

An annular denuder system was used to collect samples for the determination of ambient levels of HNO_3, SO_2, NH_3 and particulate nitrate during a 10-day study. The HNO_3 and NO_3^- measurements were compared to similar measurements made with a denuder difference measurement.

Replicate air quality data obtained with ADM systems for SO_2 and HNO_3 demonstrated that the reproducibility of the ADM was ± 0.16 μg/m^3 for SO_2 and ± 0.05 μg/m^3 for HNO_3. Since the volume of air sampled by the DDM was 1/15 that of the ADM, we could only reasonably compare results of the ADM and DDM when the concentrations of HNO_3 were > ~/μg/m^3. Based on this criteria the DDM and ADM provided data for HNO_3 which was in reasonable agreement when the HNO_3 concentrations were above 1 μg/m^3 and sampling periods were equal to or greater than 12 hours.

A sample collection system based on annular denuders followed by particulate filters appears to be a very promising system for measurement of HNO_3, NO_3^-, SO_2, $SO_4^=$, NH_3, NH_4^+ and H^+. The system's main features are: (a) operation at a relatively high flow rate while maintaining a collection efficiency greater than 95%; (b) use of denuder coatings which are extractable in water and compatible with conventional IC analysis; (c) single flow train and corresponding reduction in the number (and cost) of flow control devices; (d) relatively easy to set up and operate; (e) all gases of interest are removed from the sample stream by denuders prior to passage of the sample stream through any filter medium. In this configuration the acidification or neutralization of particles on filters is minimized.

References

1. Shaw, R. W., Stevens, R. K., Bowermaster, J. Tesch, J., and Tew E. (1982), "Measurements of Atmospheric Nitrate and Nitric Acid; The Denuder Difference Experiment," Atmos. Environ. 16, 845-853.

2. Possanzini, M., Febo, A., and Liberti, A. (1983) "New Design of High-Performance Denuder for the Sampling of Atmospheric Pollutants," Atmos. Environ. 17, 2605-2610.

3. Gormley, P., and Kennedy, M. (1949) "Diffusion from a Stream Flowing Through a Cylindrical Tube" Proc. R. IR. ACAD 52A 153-169.

4. Ferm, M. (1979) "Method for the Determination of Atmospheric Ammonia," Atmos. Environ. 13, 1385-1393.

5. Sjödin, A. and Ferm, M. (1985) "Measurements of Nitrous Acid in an Urban Area," Atmos. Environ., in press.

6. Ferm, M. and Sjödin, A. (1985) "A Sodium Carbonate Coated Denuder for Determination of Nitrous Acid in the Atmosphere," Atmos. Environ., in press.

7. Stevens, R.K., Dzubay, T.G., Russwurm, G.M. and Rickel, D. (1978) "Sampling and Analysis of Atmospheric Sulfate and Related Species," Atmos. Environ. 12, 55-68.

8. Peake, E. and Stevens, R.K., "Characterization of the Kananaskis Annular Denuder System (KAPS) to Measure Air Pollutants," In Preparation (1985).

TABLE 1

Typical Ambient Concentrations of Chemical Species Related to Acidic Dry Deposition

Gases	Concentration ($\mu g/m^3$)
SO_2	0.2 - 30
HNO_3	0.1 - 15
NO_2	0.2 - 30
HCl	0.1 - 10
HNO_2	0.2 - 2
NH_3	0.1 - 20
O_3	30 - 150
Aerosols	**Concentration ($\mu g/m^3$)**
$SO_4^=$	0.2 - 40
NO_3^-	0.1 - 10
H^+	.02 - 10
Trace Metals (elements, e.g., Na, As, Se, Pb)	.001 - 30
Organics (organic acids, agricultural pesticides, herbicides)	.001 - 30

Table 2
COMPARISON OF ADM AND DDM SYSTEMS

	ADM	DDM
Denuders:	381 x 38 mm	470 x 12 mm
Annular Space	1.5 mm	Not Applicable
Coating:	Na_2CO_3: glycerine	MgO
Flow Rate:	15 LPM	2 LPM
Filters:	47 mm 2 µm Teflon 47 mm 1 µm Nylon	25 mm 1 µm Nylon 47 mm 2 µm Teflon 47 mm 1 µm Nylon 47 mm glass fiber treated with TEA
Species Measured:	HNO_3, SO_2, NO_3^-, $SO_4^=$ NH_3, (HNO_2), (H^+)	HNO_3, NO_3^-, $SO_4^=$, SO_2, NO_2
Analysis:	IC, Colorimetry	IC

TABLE 3
ITALY - USA FIELD STUDY, RTP, NC -- SPRING 1985
REPLICATE ADM TEST

SO_2

DATE	MEASUREMENT, μg/m³ 1	2	%	Average
3/27 - Day	6.44	6.44	0.0	6.44
3/27 - Night	2.84	3.13	4.8	2.98
3/29 - Day	4.69	4.49	2.2	4.59
3/29 - Night	5.00	4.40	6.4	4.70
3/30 - Day	3.87	3.68	2.5	3.77
3/30 - Night	5.01	4.56	4.7	4.78
3/31 - Day	1.11	1.43	12.6	1.27
3/31 - Night	2.61	2.30	6.3	2.45
4/1 - Day	2.45	2.85	7.5	2.65
4/1 - Night	3.90	3.42	6.5	3.66
Average			5.4±3.7	

HNO_3

DATE	MEASUREMENT, μg/m³ 1	2	%	Average
3/27 - Day	1.55	1.47	2.7	1.51
3/27 - Night	0.55	0.63	6.8	0.59
3/29 - Day	1.57	1.55	0.6	1.56
3/29 - Night	0.71	0.62	6.8	0.66
3/30 - Day	1.02	1.00	1.0	1.01
3/30 - Night	0.66	0.63	2.3	0.64
3/31 - Day	1.26	1.36	3.8	1.31
3/31 - Night	0.34	0.35	1.4	0.35
4/1 - Day	0.58	0.52	5.4	0.55
4/1 - Night	0.16	0.14	6.7	0.15
Average			3.8±2.5	

Table 4

RESULTS OF DDM VS. ADM FOR AMBIENT CONCENTRATIONS OF HNO_3
($\mu g/m^3$)

DATE	DDM	ADM
	12 Hour Experiment	
3/28	0.78	0.78
3/29	1.31	1.11
4/1	0.29	0.35
4/2	0.84	0.77
	24 Hour Experiment	
3/29	1.54	1.56
3/30	0.96	1.01
4/1	0.85	0.55

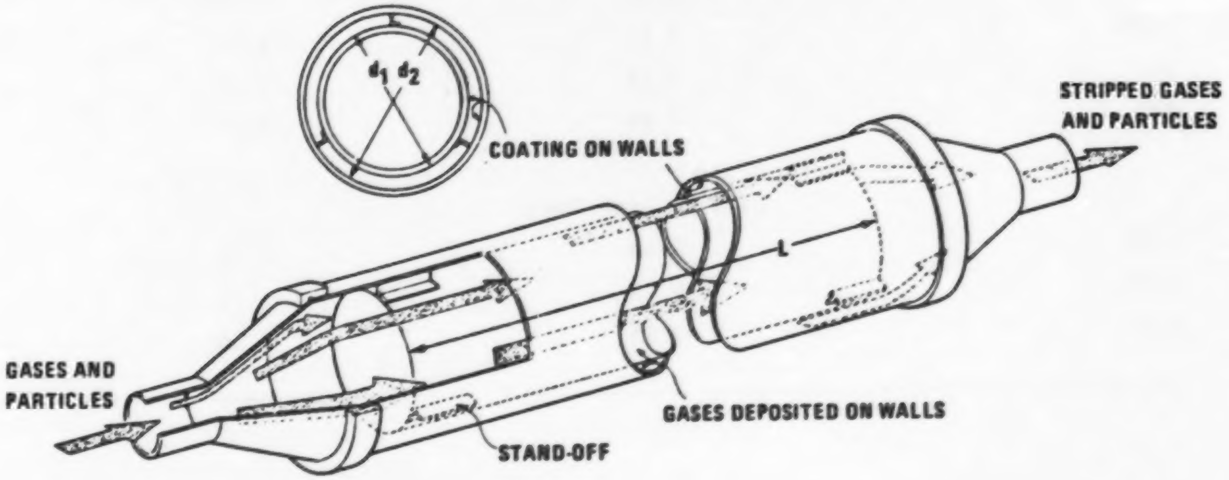

d1 d2
COATING ON WALLS
STRIPPED GASES AND PARTICLES
L
GASES AND PARTICLES
GASES DEPOSITED ON WALLS
STAND-OFF

Figure 1 **ANNULAR DENUDER**

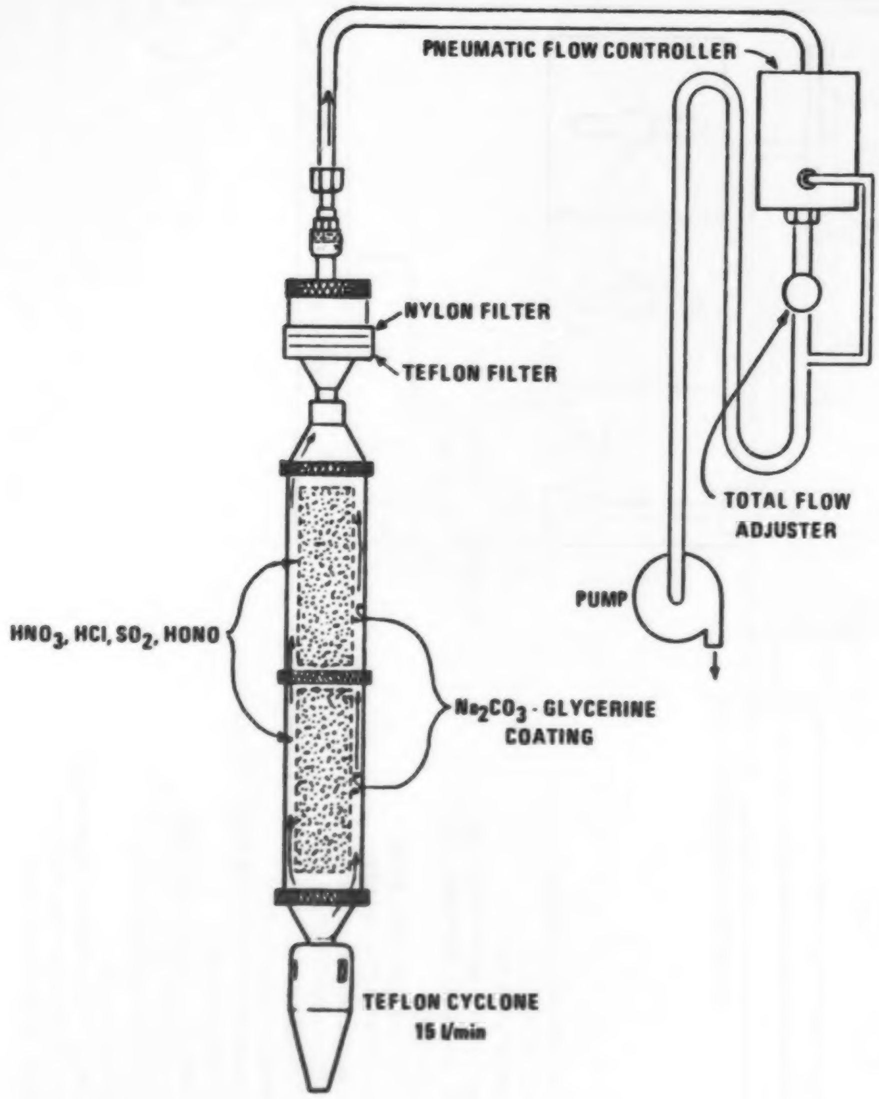

PNEUMATIC FLOW CONTROLLER
NYLON FILTER
TEFLON FILTER
TOTAL FLOW ADJUSTER
PUMP
HNO$_3$, HCl, SO$_2$, HONO
Na$_2$CO$_3$ - GLYCERINE COATING
TEFLON CYCLONE 15 l/min

Figure 2. Main components for annular denuder method (ADM): a filter pack system used to collect HNO_3, HCl, SO_2, NO_3^-, HONO, $SO_4^=$, and H^+.

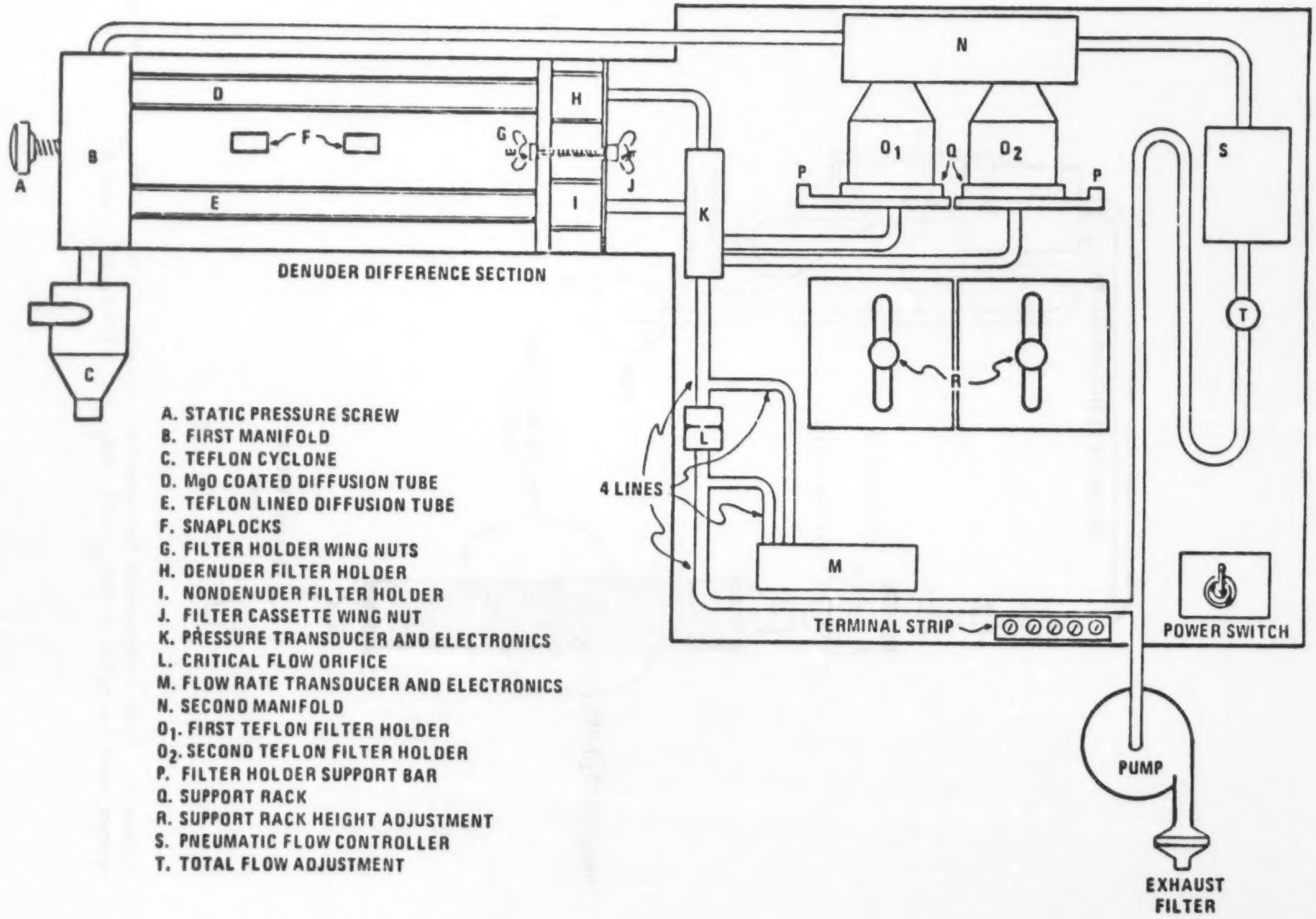
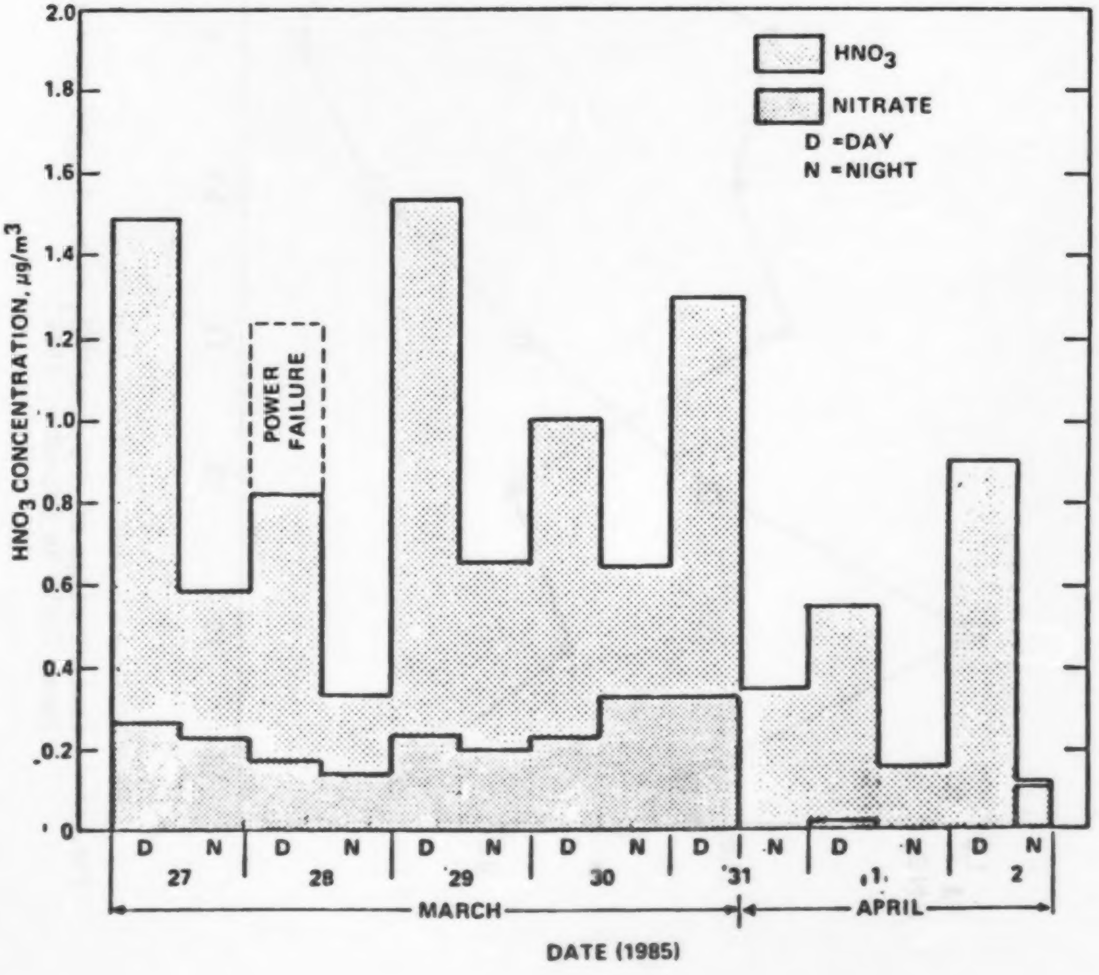

A
B
C
D
E
F
G
H
I
J
K
L
M
N
O1
O2
P
P
Q
R
S
T
DENUDER DIFFERENCE SECTION
4 LINES
TERMINAL STRIP
POWER SWITCH
PUMP
EXHAUST FILTER
A. STATIC PRESSURE SCREW
B. FIRST MANIFOLD
C. TEFLON CYCLONE
D. MgO COATED DIFFUSION TUBE
E. TEFLON LINED DIFFUSION TUBE
F. SNAPLOCKS
G. FILTER HOLDER WING NUTS
H. DENUDER FILTER HOLDER
I. NONDENUDER FILTER HOLDER
J. FILTER CASSETTE WING NUT
K. PRESSURE TRANSDUCER AND ELECTRONICS
L. CRITICAL FLOW ORIFICE
M. FLOW RATE TRANSDUCER AND ELECTRONICS
N. SECOND MANIFOLD
O1. FIRST TEFLON FILTER HOLDER
O2. SECOND TEFLON FILTER HOLDER
P. FILTER HOLDER SUPPORT BAR
Q. SUPPORT RACK
R. SUPPORT RACK HEIGHT ADJUSTMENT
S. PNEUMATIC FLOW CONTROLLER
T. TOTAL FLOW ADJUSTMENT

Figure 3. Main components of nitric acid denuder difference method (DDM) and fine particle sampler.

Figure 4
DIURNAL VARIATION IN NITRATE CONCENTRATION, RALEIGH, NC, 1985



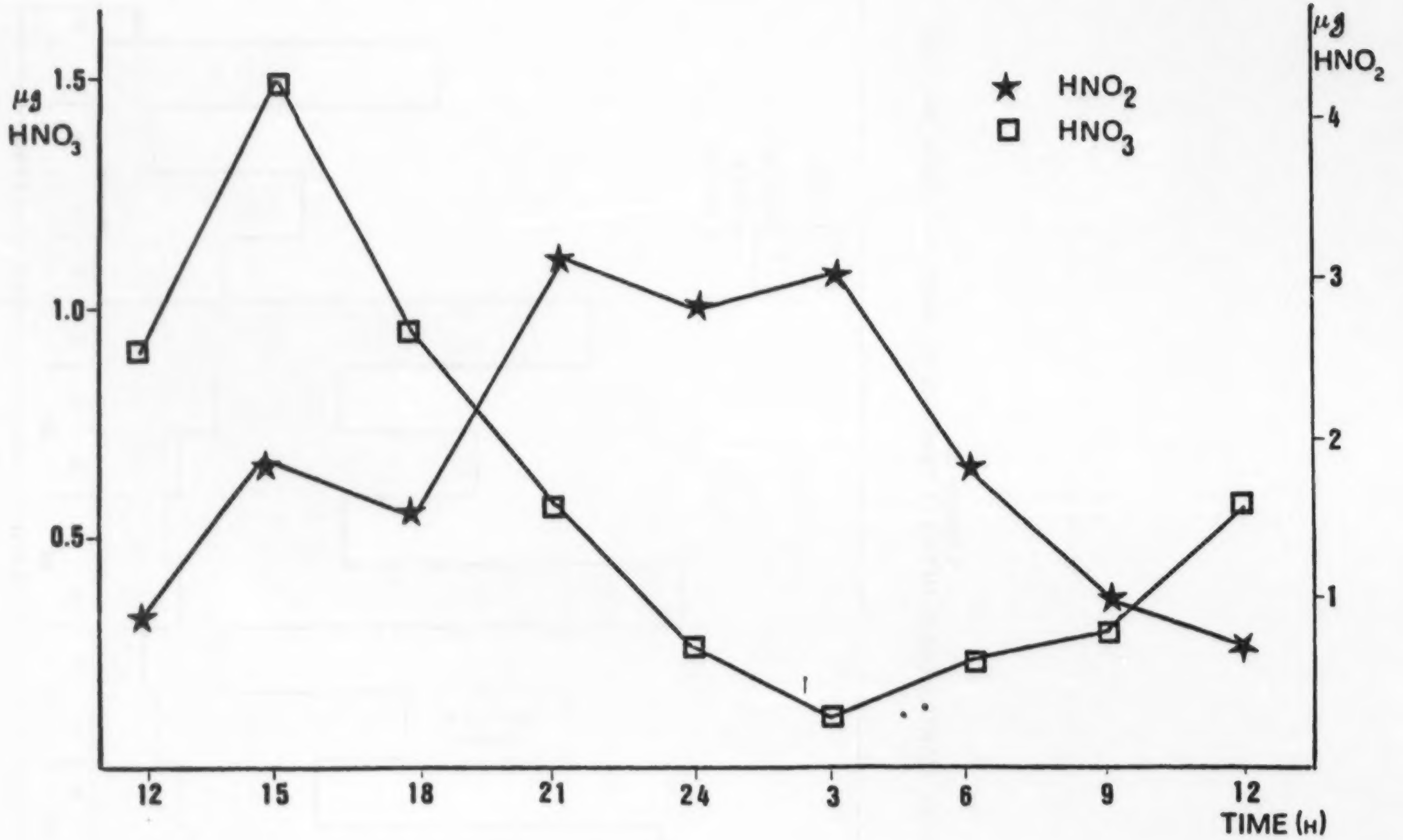


Fig. 5 Concentration of HNO_2 and HNO_3 every 3 hours over a 24-hour sampling period in Rome, Italy in February, 1985.

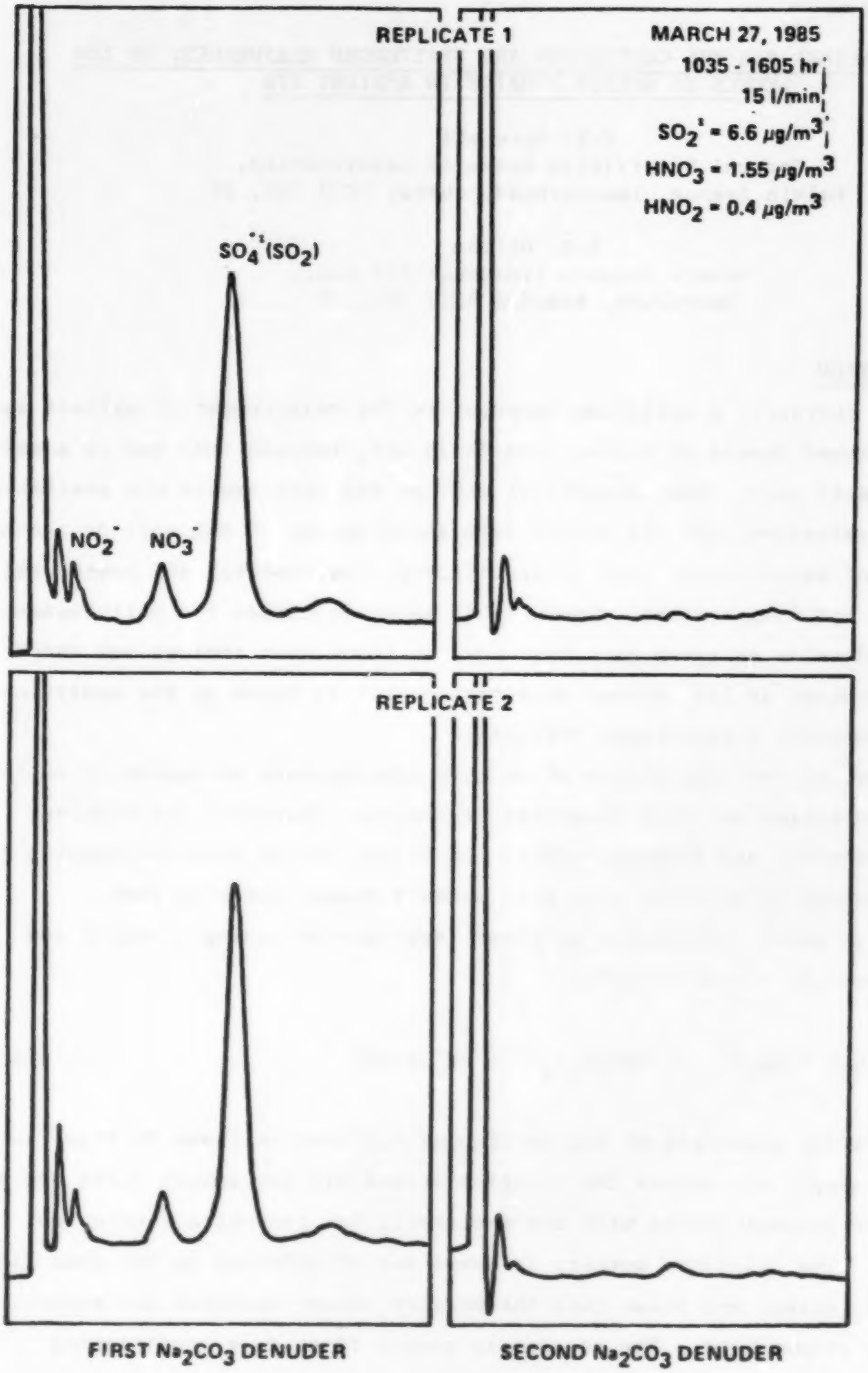


Fig. 6. Typical ion chromatogram of parallel annular denuders which have collected ambient air samples. The second denuder after the first denuder does not contain measurable amounts of $SO_4^=$ or NO_3^- indicating the efficiency of the first denuder.

A NEW ANALYSER FOR THE CONTINUOUS AND UNATTENDED MEASUREMENT OF LOW LEVELS OF SULFUR DIOXIDE IN AMBIENT AIR

G.B. Marshall
Central Electricity Research Laboratories,
Kelvin Avenue, Leatherhead, Surrey KT22 7SE, UK

D.A. Hilton
Severn Science (Instruments) Ltd.,
Thornbury, Bristol BS12 2UL, UK

1. INTRODUCTION

There is currently a worldwide interest in the measurement of ambient and natural background levels of sulfur dioxide in air, because this gas is a major precursor to acid rain. Many analytical methods and instruments are available for this determination, but all suffer from shortcomings of one sort or another such as lack of sensitivity, lack of specificity, instrumental and procedural complications and long response times. This paper describes the performance of a new sulfur dioxide analyser free from most of these shortcomings and whose principal advantage is its extreme sensitivity. It is based on the analytical technique of Mercury Displacement Detection.

The theory of the application of mercury displacement detection to sulfur dioxide determination has been described previously, (Marshall and Midgley, 1981 , and Marshall and Midgley, 1982). In brief, sulfur dioxide promotes the disproportionation of mercury(I) to give mercury vapour which is then determined with great sensitivity by atomic spectroscopy using a simple and inexpensive mercury vapour detector.

$$2SO_2 + 2H_2O + Hg_2^{2+} \rightarrow Hg(SO_3)_2^{2-} + Hg^{\circ} + 4H^{+} \qquad \ldots (1)$$

The operating principle of the continuous analyser is shown in Figs. 1a and 1b. The sample air enters the reaction vessel via the sample inlet and any sulfur dioxide present reacts with the mercury(I) ion reagent according to reaction (1). The liberated mercury is swept out of solution by the same flow of sample air, dried, and drawn into the mercury vapour detector for atomic spectroscopic measurement. The reagent is pumped first to a conditioning vessel, where sulfur dioxide free air is continuously bubbled through to reduce the blank, and then to the reaction vessel and finally to waste. The instrument is calibrated by passing known concentrations of sulfur dioxide in air from a permeation tube calibrator through the apparatus in place of the sample air.

2. PERFORMANCE

At the start of the design work a performance specification was set for the instrument and this is shown in the first column of Table 1. The second column shows the actual performance of the analyser. In all cases the specification was met. The definitions of the various parameters are those of EPA (1979).

The instrument is programmed to operate continuously without operator attention on a pre-set cycle of zero, calibrate and measure. The frequency of zero and calibrate checks depends on the accuracy and precision required. When the instrument was operating on zero for 10 minutes, calibrate for 10 minutes, and sample for 60 minutes (which is the most frequent zero and calibrate check envisaged), maximum zero drift was as little as 0.21 ppb between zero checks. Over a 12 hour period the maximum zero drift (calculated as the maximum change of continuous output response) was observed as 0.68 ppb, over a 24 hour period the net change in response was 0.49 ppb. The stability of the instrument to continuous inputs of sulfur dioxide is demonstrated by the span drift results, where over two separate periods of 24 hours first 20 ppb SO_2 and then 80 ppb SO_2 were passed continuously to the instrument. The net changes in response to these levels of SO_2 over 24 hours were 0.41 ppb and 2.85 ppb respectively. These results confirm the inherent stability of the instrument particularly when it is remembered that the span drift results include errors introduced by the permeation tube calibrators.

The instrument is linear over three orders of magnitude, i.e. from its limit of detection to 100 ppb. Should higher levels of sulfur dioxide than this be required to be measured the incoming sample should be diluted by an appropriate amount.

The instrument proved to be of high precision - at 20 ppb and 80 ppb sulfur dioxide relative standard deviations of 0.66% and 0.76% were calculated. This was confirmed by a low level precision test where relative standard deviations of 1.5% and 1.3% were recorded for 7.2 and 11.0 ppb sulfur dioxide. Again it should be emphasized that these values include errors introduced by variability in the permeation tube calibrators.

The instrument responds rapidly to changes in sulfur dioxide concentration, i.e. 1.5 minutes to 95% of final concentration. More rapid response times for special applications can be obtained by increasing the air flow through the analyser (at the expense of a reduced concentration range) or by increasing the temperature of the reagents.

The length of time the analyser is able to run without attention is determined by the volume of solution in the reagent reservoir. A 20 litre supply enables continuous running for 22 days. The maximum time of unattended operation is determined by the reliability of the peristaltic pump tubes.

3. DISCUSSION

The principal advantage of the instrument is its extreme sensitivity and consequent ability to analyse true background levels. This is demonstrated by its lower detectable limit of 0.12 ppb. Sulfur dioxide analysers based on flame photometry or molecular fluorescence do not have this inherent sensitivity.

The instrument has good selectivity since it does not respond to other species present in the atmosphere (Marshall and Midgley, 1981). Of special importance in speciation studies is its lack of response to sulphate since it is advantageous to distinguish sulfur dioxide from particulate sulphate.

The instrument is safe to use - requiring no flammable gases and there is no hazard from the dilute Hg(I) solution used or from the minute quantities of mercury vapour released by the reaction.

If modified in a minor way the instrument is able to measure sulfite ion continuously in aqueous solution. This is achieved by replacing the sample air with a sulfur dioxide free carrier gas and feeding the sulfite solution directly to the reagent in the reaction vessel through an additional entrance port. This application could be extremely useful in environmental studies where speciation is required between sulfite ion and sulfate ion in rain water, cloud water etc.

The instrument is available commercially, being made under CEGB licence.

4. ACKNOWLEDGEMENT

This work is published by permission of the Central Electricity Generating Board.

TABLE 1: INSTRUMENT PERFORMANCE CHARACTERISTICS

Performance Parameter	Specification	Actual Performance
Unattended Operation	10 days	✓
Lower Range	0 to 100 ppb	✓
Lower Detectable Limit	0.2 ppb	0.12 ppb
Noise (1) Base Line	0.1 ppb	0.06 ppb
(2) 80% Upper Range Limit (URL)	1% of concentration (0.8 ppb)	0.30 ppb
Zero Drift	0.2 ppb between zero checks	0.21 ppb
Span Drift (1) 20% URL	5% of concentration (1.0 ppb)	0.41 ppb
(2) 80% URL	5% of concentration (4.0 ppb)	2.85 ppb
Response Time (1) Lag Time	15 s	8 s
(2) Rise Time	1.5 min	1.5 min
(3) Fall Time	2 min	2 min
Precision (1) 20% URL	5% of concentration	0.66% r.s.d.
(2) 80% URL	5% of concentration	0.76% r.s.d.

5. REFERENCES

1. Marshall, G.B., and Midgley, D., 1981, Mercury Displacement Detection for the Determination of Picogram Amounts of Sulfite Ion or Sulfur Dioxide by Atomic Spectrometry, Analytical Chemistry, 53, 1760

2. Marshall, G.B. and Midgley, D., 1982, Continuous Atomic Spectrometric Measurement of Ambient Levels of Sulfur Dioxide in Air by Mercury Displacement Detection, Analytical Chemistry, 54, 1490

3. EPA, 1979, "Summary of Performance Test Results and Comparative Data for Designated Equivalent Methods for SO_2; Research Triangle Park, NC, Document No. QAD/M-79.12

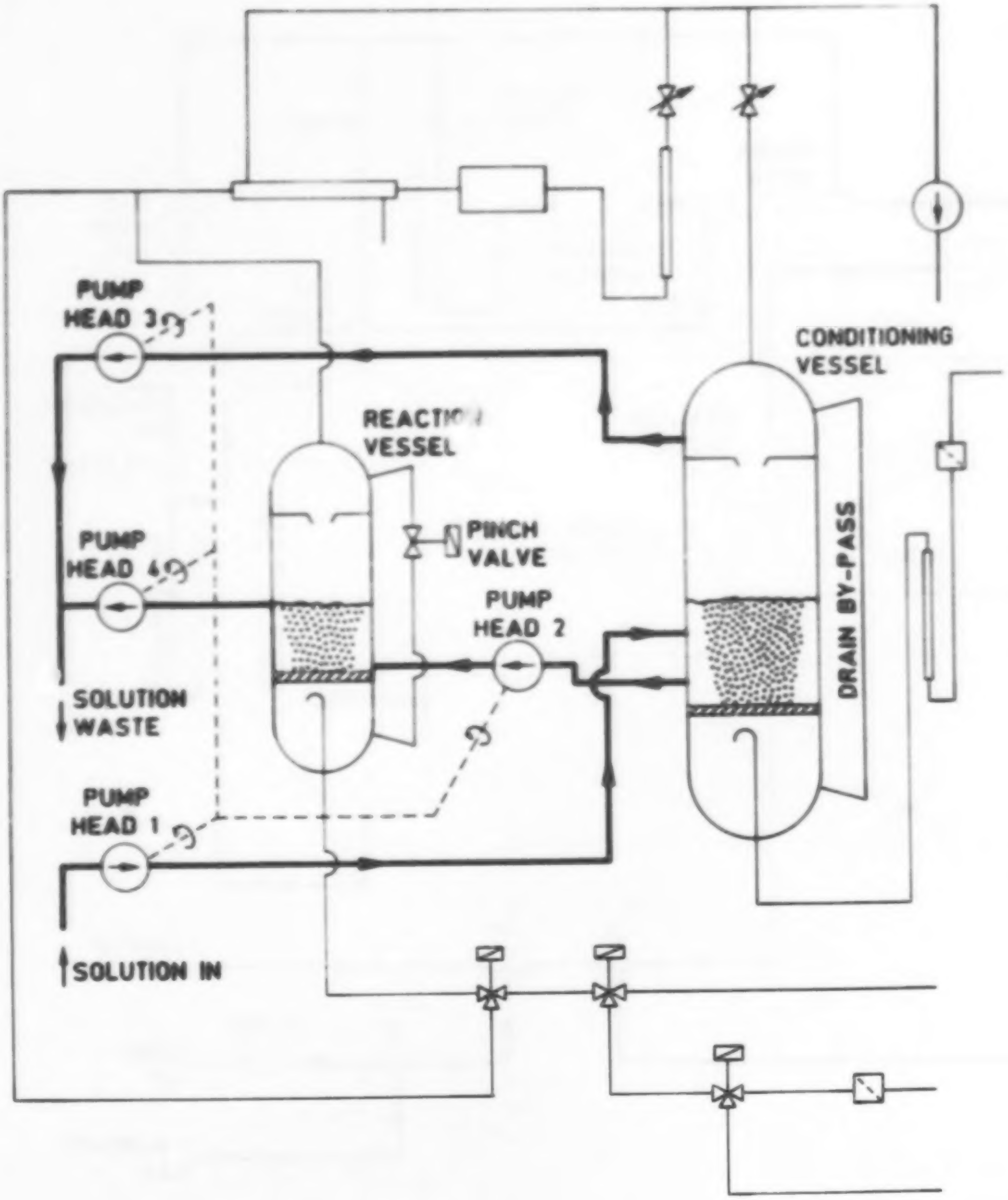

PUMP HEAD 3
CONDITIONING VESSEL
REACTION VESSEL
PINCH VALVE
PUMP HEAD 4
PUMP HEAD 2
DRAIN BY-PASS
SOLUTION WASTE
PUMP HEAD 1
SOLUTION IN

FIG. 1a SOLUTION FLOW

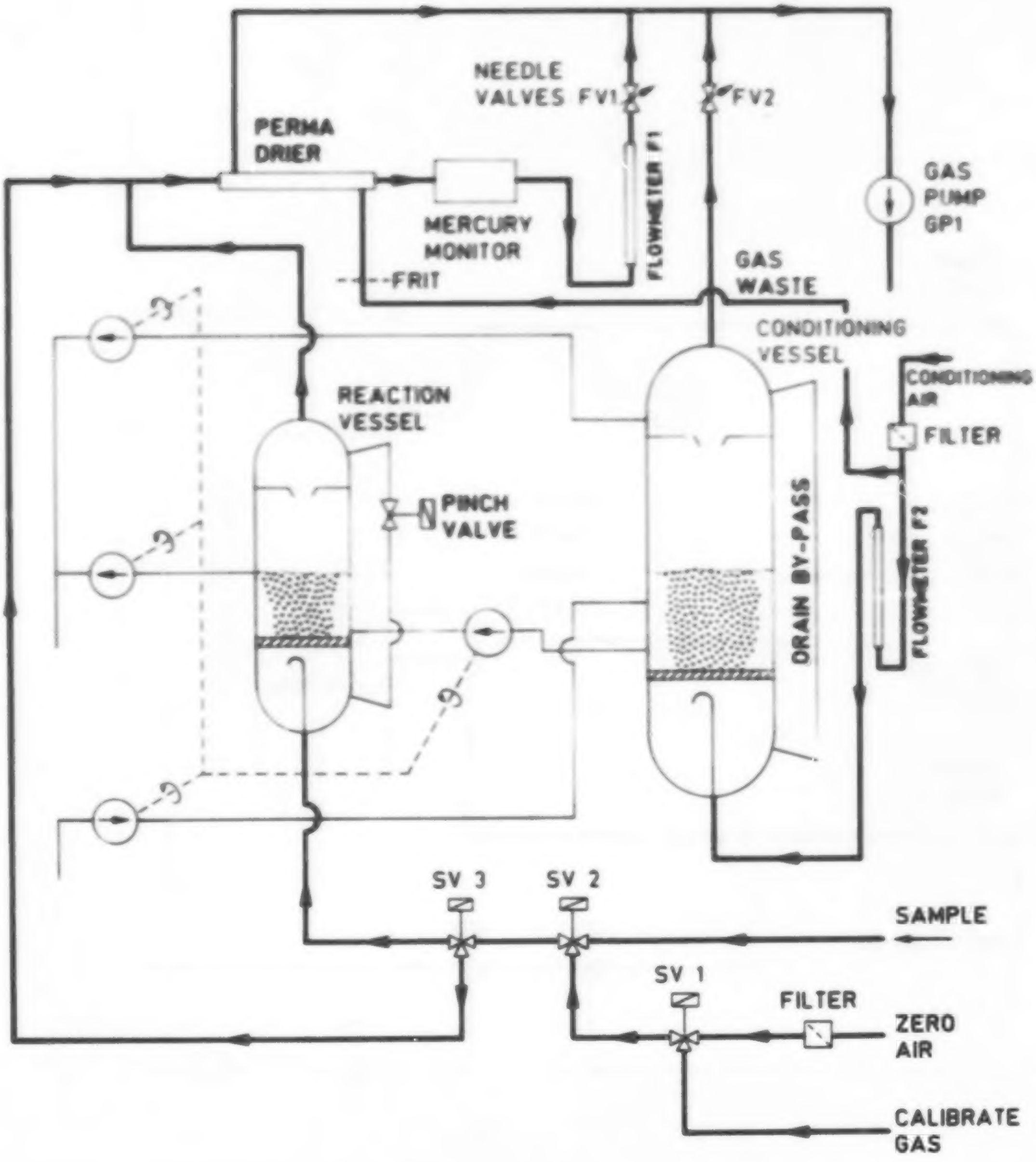

NEEDLE VALVES FV1
FV2
PERMA DRIER
GAS PUMP GP1
MERCURY MONITOR
FLOWMETER F1
FRIT
GAS WASTE
CONDITIONING VESSEL
CONDITIONING AIR
FILTER
REACTION VESSEL
PINCH VALVE
DRAIN BY-PASS
FLOWMETER F2
SV 3
SV 2
SAMPLE
SV 1
FILTER
ZERO AIR
CALIBRATE GAS

FIG. 15 GAS FLOW

ALKALINITY MEASUREMENTS IN EVALUATING HI-VOL FILTER PERFORMANCE

Rita M. Harrell and John C. Holland
Northrop Services, Inc.
Environmental Sciences
P.O. Box 12313
Research Triangle Park, NC 27709

Alkalinity measurement is a useful tool in the performance evaluation of hi-volume air filters. It is significant because alkaline sites react with SO_2 and HNO_3 in the air forming sulfate and nitrate on the filters. Such sulfates and nitrates are indistinguishable from particulate sulfate and nitrate collected by the filters. In turn, the total particulate weight, sulfate content, and nitrate content determined would be falsely high in proportion to filter alkalinity.

Alkalinity of older filters are measured in order to evaluate appropriate correction factors for previously obtained particulate data. New filters are tested for compliance with EPA specifications and determination of correction factors for the current air pollution data base.

Among the two or three laboratories, across the country, that have been involved in alkalinity measurement, a reproducibility problem has been observed using the standard method ASTM D202[1]. In part, this may be due to slight differences in each laboratory's interpretation of ASTM D202 but the major differences observed can be attributed to factors which influence alkalinity values obtained. Because of this problem, a study was initiated to investigate factors having the potential of influencing observed filter alkalinity values and to develop a simple, reproducible method for alkalinity measurement. Bruce Appel[2] has also done extensive work in this area.

From the study it was found that many factors such as extraction volume, extraction time, stirring method and filtration temperature influence alkalinity measurement. Extraction time in conjunction with extraction volume was found to produce the most significant change in alkalinity. Magnetic stirring with a 2" stirrer bar versus high speed mechanical agitation produced the least significant change.

On the basis of the overall results, of the study, a modified alkalinity measurement procedure will be recommended upon completion of interlaboratory and intralaboratory testing of the proposed method. At present, within our laboratory, agreement between two different analysts is good for alkalinity evaluation of the same filters.

---

[1] "Standard Methods of Sampling and Testing Untreated Paper Used for Electrical Insulation", ASTM D202-77, in Annual Book of ASTM Standards, 39:62 (1977).

[2] B. R. Appel, E. L. Kothny, V. Ling, and J. J. Wesolowski, "Sampling and Analytical Problems in Air Pollution Monitoring Phase II", First Quarterly Progress Report, Air and Industrial Hygiene Laboratory, California Department of Health Services, 2151 Berkeley Way, Berkeley, California 94704-9908, EPA Cooperative Agreement No. CR 810798-01-0, November 1983.

A PROCEDURE FOR THE ISOLATION AND CONCENTRATION OF MILIGRAM QUANTITIES OF CARBON MONOXIDE FROM AMBIENT AIR

by

D. A. Levaggi, R. E. England And R. V. Zerrudo
Bay Area Air Quality Management District

In evaluating the non-attainment status for carbon monoxide (CO) in the San Francisco Bay Area, unexpectedly high levels in low-traffic residential areas suggested the possibility that residential wood combustion (RWC) could be contributing to the observed excesses. In this context a ^{14}C analysis of the ambient CO would indicate any CO derived from RWC, as distinct from CO derived from fossil fuel combustion in vehicles or buildings (1).

In order to isolate the milligram levels of CO needed for the ^{14}C analysis, large volumes of air, in the order 2000ℓ, must be extracted (2). The extracted CO must also be completely devoid of any carbon contamination i.e., from carbon dioxide, particulate, or gaseous hydrocarbons. This short paper will detail some of the experimental findings in the development of a sampler to accomodate the requirements stated above. As well some field data will also be presented.

The sampling train configuration is shown in Figure 1. Four major components perform the necessary tasks of the sampler, namely; 1) hydrocarbon removal, 2) carbon dioxide (CO_2) removal, 3) carbon monoxide (CO) oxidation and 4) CO_2 (formed from CO) absorption. These will be taken up separately, with appropriate experimental findings made for each. All the experimental tests were performed at room temperature and a flow rate of 5ℓ/min. This relatively high flow rate was necessary to obtain milligram levels of CO during a sampling period of eight hours. The eight hour sampling period was chosen to accommodate the National Ambient Air Standard for CO (9 ppm 8-hour average).

HYDROCARBON REMOVAL

It is well known that activated charcoal is an excellent absorber of organic gases from air streams. This removal efficiency increases with increasing molecular weight of the gas, e.g. methane and ethane at 5ℓ/min. are not absorbed and retained for any length of time. The concern, however, was the absorption and retention of C_3 and higher hydrocarbons, which had the possibility of being oxidized by the Hopcalite located downstream in the sampler. The Hopcalite oxidizing potential will be taken up separately later in the text.

Experiments were performed using blends of 1.2 ppm propane and 1.0 ppm butane in air with background methane, and 12 mesh activated coconut charcoal. The charcoal was packed in a 120cc plastic cannister. The only pretreatment of the charcoal was a purge using cylinder nitrogen at 5ℓ/min. for one hour. The experiments were monitored using a Bendix Model 8201 GC-FID instrument.

Results of the experiments were not surprising and indicated the following:

- Propane was found to initially pass thru the charcoal after 1.5 hours. At the end of 4.5 hours approximately 40% of the propane was no longer being retained. The slope of the instrument recorder indicated that after an additional 1.5 hours all the propane would have been passing thru the charcoal.
- Butane was still 100% retained after 16 hours.
- After field sampling in a highway tunnel with above ambient level hydrocarbons for 40 hours, a 120cc charge of charcoal was still removing 100% of all the C_4^+ hydrocarbons.

CARBON DIOXIDE REMOVAL

Ambient CO_2, because of its high ^{14}C content, must be removed from a sample stream by a minimum of 99.95%. Soda lime of 8-12 mesh is the primary remover of CO_2 in the sampling train. Indicating soda lime is preferred only because visual inspection immediately reveals the extent of its consumption. The soda lime is packed in two 120cc plastic cannisters placed in series, after the charcoal and prior to the ascarite-drierite filter. The ascarite (approximetely 60cc of material) is merely a back-up system should the soda lime cannisters become exhausted prior to a completed sampling run. The CO_2 removal system was found to easily accomplish the 99.95%$^+$ CO_2 removal criterion. Most experimental runs were made with approximately 20 ppm CO_2 gas streams, derived either from 20 ppm CO_2 certified cylinders or by precise dilution of a stock 2000 ppm CO_2 cylinder with zero cylinder air (no CO_2). The CO_2 content of all cylinders, generated CO_2 air streams, and the efficiency studies of the CO_2 removal portion of the sampling train were determined with a TECO Model 626. This NDIR instrument is multiranged; the sensitivity range of 0-10 ppm full scale was used routinely in the removal efficiency tests. Instrument performance was exceptional and it was felt that a lower detectable limit of 0.07 ppm CO_2 could have easily been noted. The CO_2 removal system was found to have the following characteristics:

- An eight hour ambient sample run at 5ℓ/min consumes approximate 75% of the sampling train soda lime. The two cannisters are, therefore, replenished after each 8 hour sample.
- Better than 99.95% of the incoming CO_2 is removed by the soda lime.
- Extensive field tests have shown that the ascarite containing cannister need never be replaced.

CARBON MONOXIDE OXIDATION

In order to collect the required milligram levels of CO from 2000 liters of air it is necessary to convert the CO to a collectible specie. Oxidation to CO_2 is the easiest and most conventient conversion for such a large quantity of air. Hopcalite was chosen as a likely candidate to catalize the oxidation at room temperature. This patented catalyst available from the Mine Safety Appliance Corp, has been used for many years to convert CO to CO_2 at low flow rates, and also to oxidize hydrocarbons at elevated temperatures (3, 4). Experiments then had to be performed to 1) determine if at room temperature any oxidation of C_1-C_3 took place (since the charcoal located upstream in the sampling train would remove C_4 and higher HC's and 2) to establish the oxidation efficiency of the Hopcalite for CO at an elevated flow rate, i.e. 5ℓ/min.

The need for a selective oxidation of CO is that most all airborne hydrocarbon gases originate from fossil fuel combustion. These gases contain no ^{14}C and would, therefore, bias any CO-^{14}C analysis. This bias is exactly the opposite of that which ambient CO_2 would cause.

A 3.0 ppm propane, 3.1 ppm methane standard in air was used to evaluate its oxidation by a bed of approximately 50cc of Hopcalite. The inlet and outlet of the Hopcalite were monitored with the Bendix 8201. Absolutely no difference could be detected in the hydrocarbon mixture upon its passage thru the catalyst.

In another experiment a NBS traceable CO gas mixture (10.1 ppm in air) was passed thru the Hopcalite. The exiting gas was monitored by a Bendix Model 8501 NDIR for CO and the TECO Model 626 for CO_2. CO was never detected and the CO_2 concentration was found to be 9.8 ppm, indicating a quantitative conversion of the CO to CO_2.

Experimentation and field studies indicate that:

- Hopcalite (a 50cc charge) is capable of the quantitative conversion of CO in air to CO_2, at room temperature and 5ℓ/min.
- Hopcalite does not cause any perceptible oxidation of a $C_1 + C_3$ gas mixture in air. Based on instrument detectability we estimate less than 1% oxidation, and feel confident that it is even less.
- Field sampling indicates that after twenty 8 hour runs the Hopcalite is still performing at its full $CO \longrightarrow CO_2$ efficiency.
- The Hopcalite should be dried at 100°C for two hours prior to use and desiccated. If kept dry it performs as expected.

CO COLLECTED AS CO_2

The final element of the sampling train is an absorber to collect the CO_2 which was selectively oxidized to CO_2 by the Hopcalite. The absorber contains sodium hydroxide (NaOH) which has been evenly distributed on 16-18 mesh firebrick. It was determined that a 3" x 1" drying tube packed with the treated fire brick was an effective collector of CO_2.

The absorbers must be "clean" of carbonate carbon and are prepared in a nitrogen glove box. The sodium hydroxide used to impregnate the 16-18 mesh firebrick must be carbonate free. We have used a J. T. Baker "carbonate free" product which contains 5 eq. of NaOH in about 460 ml of water in a sealed plastic bottle. The product, however, was not found to be carbonate free, and requires a pretreatment with barium chloride to render it acceptable (5). The recipe for preparation of the absorber tubes is 60 gm of firebrick to 28cc of the 5 eq solution. Details of the preparation are available on request. Ten tubes can be made from the aforementioned recipe. If prepared as described the 3" packed tubes were found to contain an acceptable 0.2 mg of carbonate carbon. To prevent contamination from ambient CO_2, the tubes, after preparation, prior to and after field sampling, are always stored in a sealed container containing liberal quantities of soda lime.

Extensive testing of prepared tubes revealed that the collection efficiency was strongly influenced by storage time. The collection efficiency is satisfactory (basically 100%) up to four days after preparation. This is not considered to be terribly disadvantageous since a batch of absorption tubes can be easily prepared in less than 1.5 hours.

MISCELLANEOUS

The Drierite located in various positions in the sampling train serves as a source of moisture removal which preserves the effectiveness of the Ascarite and Hopcalite catalyst.

Two 47mm glass fiber filters are positioned to keep the Hopcalite clean, and also remove any fines from the Hopcalite reaching the CO_2 absorber.

A detailed checkout protocol has been established for the sampling train prior to its field use. The procedure calls for a visual inspection of the chemicals used, a leak check, and verification of an active Hopcalite catalyst. The entire pre-sampling procedure takes about 20 minutes.

SUMMARY

A sampling train which will selectively separate milligram levels of ambient CO from air has been developed. It is relatively simple and inexpensive to fabricate and has been thoroughly laboratory and field tested. It should prove valuable in resolving the origin of elevated CO ambient concentrations in areas with a concomitant large percentage of homes utilizing RWC. The procedure also appears well suited to augment and/or confirm receptor modelling studies in many areas such as Vail, Missoula and Portland where large scale RWC has caused intense winter air pollution problems (6).

REFERENCES

1. Cooper, J. A., Currie, L. A. and Klouda, G. H.: "Assessment of Contemporary Carbon Combustion Source Contributions to Urban Air Particulate Levels Using Carbon-14 Measurements", Env. Sci. Techn. 15, p. 1045, (1981).

2. Jull, A. T., Donahue, D. J. and Zabel T. H.: "Target Preparation for Radiocarbon Dating by Tandem Accelerator Mass Spectrometry", Nuclear Instruments and Methods in Physics Research 218 p. 509, (1983).

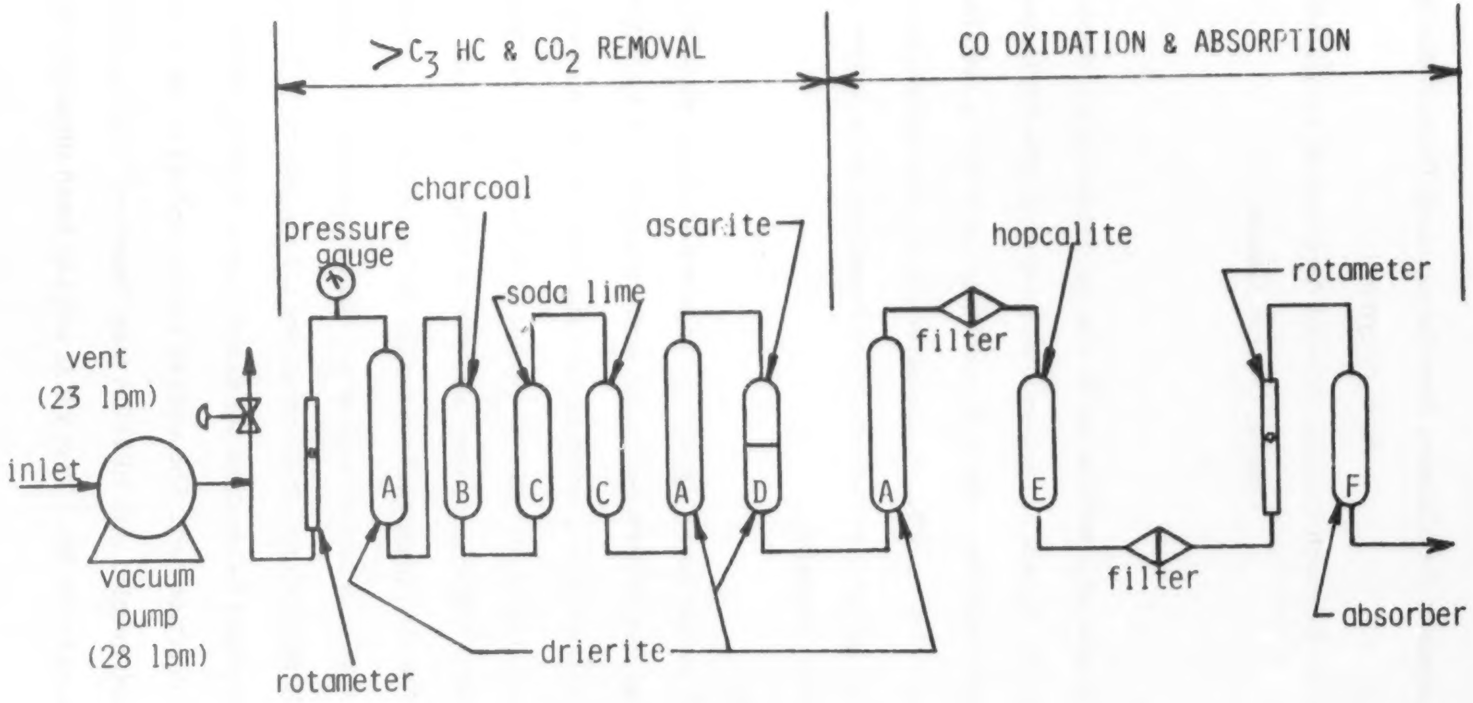
3. Lindsley, C. H., Yoe, J. H.: "Acidimetric Method for Determination of Carbon Monoxide In Air", Anal. Chem. 21 p. 513 (1949).

4. McDonough, J. P.: "Detection, Reduction and Control of Gaseous Contaminants", Mine Safety Appliances, Filter Products Div. (1978).

5. "Scotts Standard Methods of Analysis", by W. W. Scott, Fifth Ed. 1939, Edited by N. H. Furman, p. 2197, D. Van Nostrand Co., Inc. Publishers.

6. "Proceedings 1981 International Conference on Residential Solid Fuels, Environmental Impacts and Solutions", Edited by J. A. Cooper and D. Malek; Oregon Graduate Center, Beaverton Oregon, Publishers.

^{14}C SAMPLING TRAIN



$>C_3$ HC & CO_2 REMOVAL
CO OXIDATION & ABSORPTION
vent
(23 lpm)
inlet
vacuum
pump
(28 lpm)
pressure
gauge
rotameter
charcoal
soda lime
ascarite
drierite
A
B
C
C
A
D
A
filter
hopcalite
E
filter
rotameter
F
absorber

FIGURE 1

Analysis of the Effluents from Polyurethane Foam Insulation

M. E. Krzymien

National Research Council, National Aeronautical Establishment

Ottawa, Ontario, Canada

Introduction

In spite of a common belief that polyurethanes are chemically stable and do not degrade in temperatures lower than 100-200°C, there is a growing concern that they may emit decomposition products upon heating at temperatures as low as 80°C. In this paper the volatile degradation products of MDI based, rigid polyurethane foam were analyzed and a number of them were tentatively identified.

Experimental

A sample (about 2g) of rigid polyurethane foam manufactured from PMDI, sorbitol and polyethylene glycol with the addition of Syrol 6 (diecthyl aminoethyl phosphate) as a fire retardant and Freon 11 as a blowing agent, was placed in an aluminum tube and maintained at 80°C in either nitrogen or Zero Air atmosphere. These gases were also used as effluent carriers.

The off-gas samples were collected by passing the carrier gas leaving the aluminum tube through an ice coaled adsorber. The adsorber was a glass tube (75 mm x 63 mm O.D.) containing a 2-cm column of Tenax TA 35/60 mesh. For capillary GC analysis the samples were thermally desorbed in a modified (1) injection port. The analysis was carried out on HP 5790A gas chromatograph coupled with HP5970A Mass Selective Detector (MSD). The GC was operated with DB-5 30 m x 0.32 mm I.D. fused silica column.

The Mass spectra produced by MSD were identified using the Mass Spectral Identification, Probability Based Matching System (PBM) developed at Cornell University and Cornell's IBM VM 370 computer.

The mass spectral identification of the off-gases was supplemented by dual-detection gas chromatographic analysis. The analysis was performed on Varian 4600 gas chromatograph equipped with flame ionization (FID), electron capture (ECD) and thermoionic specific (TSD) detectors. The detectors were operated either individually or in pairs. The Varian GC was fitted with 30 m x 0.32 mm I.D. SPB-5 fused silica column.

Results and Discussions

Before analysis, the polyurethane foam sample was stripped of adsorbed contaminants by heating it in a stream of high purity carrier for a few days. The decontaminated sample was then heated in either high purity nitrogen or Zero Air-atmosphere without flow for several days to allow the concentration of the genuine off-gases to reach a measurable level. The effluents from such "recharged" foam are decomposition products of the foam and/or additives used in the production process such as catalysts, blowing agent, residual unreacted monomers, fire retardant, etc. Their concentrations also decrease with time at a rate depending on a carrier flow rate and their emission rates. The dependence might be used to calculate the emission rates.

It was observed that, whereas composition of the off-gas mixture did not change drastically with a change of carrier gas from nitrogen to zero air, the emission rates were significantly higher in a Zero Air atmosphere.

The individual components of the mixture were identified by GC/MSD analysis. The obtained mass spectra were compared with the reference spectra listed in spectral library. Table I lists the compounds identified by the PBM system in the PUF effluents separated on an HP 5790 gas chromatograph. Columns 6 and 7 of the table list class 4 (CL 4) and class I (CL 1) reliability of a match expressed in percentages. Class 4 reliability means the probability that the unknown compound has a structure closely related to that of the retrieved compound. Class 1 is the probability that the unknown has an identical structure (or stereoisomer) to that of the retrieved compound.

The dual-channel, dual-detector gas chromatographic analysis provided an additional qualitative information by identifying compounds as members of a group of compounds sensitive to a particular detector. For example an unknown was identified as a hydrocarbon, halocarbon, amine, nitro-compound etc.

As a result of this work over twenty compounds were tentatively identified as probable polyurethane foam off-gases. Their identity will be finally confirmed by comparison of their retention data and mass spectra with those of standard compounds.

Reference

1) M. E. Krzymien, Dual Adsorber-Capillary Column System for Gas Chromatographie Analysis of Air Samples. NRC, NAE-AN-20, 1983.

TABLE 1

PEAKS TENTATIVELY IDENTIFIED BY PROBABILITY BASED MATCHING SYSTEM (PBM)

Spectrum No.	Name	Atmosphere	R.T.	R.A. %	Reliability	
					CL4	CL1
31	Cyclohexanone	air, N_2	12.50	29.5	78	47
32	3-Methylene pentane	air, N_2	13.12	15.6	52	22
33	Unknown	air	13.66	2.0		
34	Heptanol	air, N_2	13.84	34.8	74	40
35	Cyclohexanamine (Polycat 8)	air, N_2	14.04	75.1	55	24
36	2-Phenyl propene	air, N_2	14.12	31.1	95	69
37	Octamethyl cyclotetrasiloxane (?)	air	14.22	2.9	33	13
38	Trimethyl benzene	air	14.34	5.2	80	50
39	1-Hexene	air	14.42	2.9	60	27
40	Unknown (hydrocarbon or alcohol)	air	14.86	5.1		
41	Unknown	air	15.04	2.1		
44	1-Octanol (?)	air	15.58	3.4	39	17
45	Phenyl methyl ketone	air, N_2	15.62	13.2	66	32
46	n-Nonyl aldehyde	air, N_2	16.16	14.3	77	47
47	2-Pentenal	air	16.34	5.8	53	23
48	4-Pentenal	air	16.54	7.8	60	27
49	1-Heptene	air, N_2	16.60	26.5	66	32
50	Butyl isocyanate (?)	air	17.16	3.8	35	14
51	Nonyl alcohol	air, N_2	17.24	49.7	76	44
53	Unknown (aldehyde or ketone)	air	17.62	8.8		
54	Dodecanol (?)	air	17.84	3.9	57	25
55	Methyl methylbenzoate	air	18.10	7.9	60	27
56	n-Octanol (?)	air	18.22	3.2	50	21
67	Trichlorofluoromethane (freon 11)	air, N_2	5.66	95.5	41	17
68	Trichlorofluoromethane (freon 11)	air, N_2	5.70	100.0	41	17
69	Unknown	air, N_2	6.76	5.9		
70	Methyl ethyl ketone (?)	air, N_2	6.94	12.6	43	18
71	Unknown	air, N_2	7.04	18.0		
75	Cyclohexene (tetrahydrobenzene)	air, N_2	8.00	12.9	92	61

The following paper was presented at the U.S. E.P.A. Fifth Annual National Symposium on Recent Advances in the Measurement of Air Pollutants held in April, 1985, Raleigh, North Carolina.

Richard T. McNerney, Jerome Instrument Corporation's Sales & Marketing Department

QUANTITATIVE ANALYSIS OF PPB CONCENTRATIONS OF HYDROGEN SULFIDE IN AIR USING A GOLD FILM SENSOR

In 1972, a new sensor was developed for the detection of nanogram quantities of elemental mercury. This sensor, which received a U.S. patent in 1976, is a thin gold film prepared by high vacuum evaporation on a ceramic substrate.

Previous to the development of the thin gold film, instruments for the determination of mercury relied mainly on the atomic absorption (AA) technique. However, the AA technique has serious limitations in terms of selectivity and sensitivity to mercury.

Instruments using the Gold Film technique for mercury detection overcame these limitations and now enjoy a worldwide acceptance for industrial hygiene surveys, environmental studies, and precious metal and geothermal prospecting. Several articles detailing the gold film and the instruments which utilize this sensor have appeared in Science, Analytical Chemistry, American Laboratory, and several geologic journals. Reprints of these papers are available from Jerome Instrument Corporation upon request.

In the 1972 Science article entitled "Mercury Detection by Means of Thin Gold Films," it was stated "...in exploratory experiments we have investigated the applicability of measuring other gases. The gold film is at least as sensitive to H_2S (hydrogen sulfide) as it is to Hg, and so it can potentially serve as an H_2S detector."

In the development of the Gold Film Mercury Analyzers, an intake filter consisting of mallcosorb was necessary to eliminate ambient levels of hydrogen sulfide. And, it was the Gold Film sensor's response to these very low hydrogen sulfide concentrations that prompted our R & D effort, beginning in 1982, and culminating in April of this year; this effort led to the development of an instrument capable of the part per billion determination of H_2S in air.

The sensor detects hydrogen sulfide by adsorbing H_2S on its surface. This results in an increase in electrical resistance of the gold film; this resistance change is measured by incorporating a sensor and a reference film in a Wheatstone bridge circuit. The mechanism for the resistance change on the thin gold film is thought to be an impedance of conduction electrons due to the adsorption of hydrogen sulfide on the surface.

The reaction that takes place on the gold film in the presence of hydrogen sulfide is given by the equation: $Au + H_2S \longrightarrow AuS + H_2\uparrow$. It is the formation of this gold sulfide layer on the surface that results in the change in electrical resistance of the film. The reaction is reversible and in practice the sensor is regenerated periodically by means of a thin film heater that is sandwiched between the sensor and reference. The thermal regeneration of the sensor is given by the equation: $AuS + O_2 \xrightarrow{heat} Au + SO_2\uparrow$. Studies have shown that sensor regeneration in the absence of O_2 will not remove the gold sulfide layer.

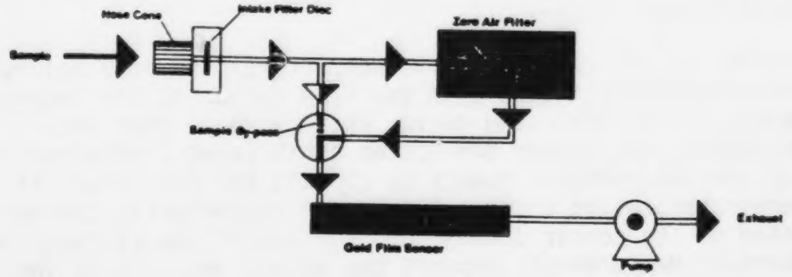
The first one and one-half years of R & D effort were directed toward the refinement of the Gold Film sensor. As previously mentioned, the sensor used in the mercury analyzers was sensitive to H_2S, but its response to H_2S would degrade with time.

The new sensor underwent several chemical and physical changes - changes which cannot be addressed here because of their proprietary nature. This sensor proved to be even more sensitive to hydrogen sulfide and exhibited excellent stability. The sensor was also reduced in physical size to that of a large postage stamp.

Since the Gold Film sensor accurately measures picogram quantities of hydrogen sulfide, a small volume of sample (typically less than 1cc) is required for ppb level analysis. Therefore, the next phase of the R & D effort was the development of a sampling system that would accurately deliver a minute sample volume of gas, yet be small and rugged enough to be contained in a portable instrument. Also, since the instrument can be operated as a continuous, fixed point monitor, the sensor regeneration cycle necessitated the delivery of "zero air" to the sensor during this cycle, especially when operating in an atmosphere containing H_2S.

The sample delivery system developed consists of the following major components: dust filter, solenoid, zero air filter, and pump. The internal pump draws the sample through the zero air filter. This filter, made of iodine impregnated charcoal, removes any hydrogen sulfide from the sample. At a predetermined time, the solenoid is activated, diverting a sample directly to the Gold Film sensor. The H_2S in this sample is adsorbed and integrated by the Gold Film sensor. The solenoid closes, resuming the sample flow through the zero air filter. The volume of actual sample delivered to the sensor can be varied from 1/4 cc to 25 cc.

GAS FLOW SCHEMATIC



There is a finite number of adsorption sites on the surface of the Gold Film sensor. As sulfur atoms use up these sites, the response will gradually decay due to a decrease in adsorption efficiency by the sensor. The final phase of the R & D effort was the development of microprocessor based electronics with support software in order to compensate for this cumulative loss of sensitivity (non-linearity).

This electronic package handles all of the high tolerance timing and sequencing functions demanded by the sample delivery system. The microprocessor automatically compensates for the non-linearity of the sensor as well as the individual characteristics of each Gold Film sensor. Also designed into the system were non-volatile memory devices and supporting software programs that would allow the operator to (1) automatically recalibrate the instrument with no internal adjustments, (2) change the timing of the sample sequencing system, and (3) operate the instrument as a fixed point, continuous monitor.

The automated calibration software is a menu-driven program that allows the operator to calibrate the instrument precisely to a calibration gas. In this program, the operator has the option of resetting two timing functions, called sample wait times, in the sample delivery system. The "1st Sample Wait Time" is the 'Pump on - sample through the zero air filter' sequence. This can be adjusted from 2 to 10 seconds in order to allow for the delivery of a sample from a remote location or for injection of a sample by syringe - a typical procedure for headspace analysis. For most applications, however, the optimum time is 5 seconds. The "2nd Sample Wait Time" is the 'Solenoid open - close' sequence; a sample is delivered to the Gold Film sensor, bypassing the zero air filter. This timing function can be varied from 0.1 to 9.9 seconds. It is this function that allows the operator to adjust the sample volume to the expected hydrogen sulfide concentration in order to maximize precision and accuracy. Studies have shown that a 0.5 second solenoid open time gives excellent reproducibility for H_2S concentrations from 10 to 500 ppb, whereas a 5 second solenoid open time is optimum for expected H_2S concentrations less than 10 ppb. In this way, the Gold Film sensor adsorbs the same mass of hydrogen sulfide from a sample; thus, the electronic signal produced would be similar whether one is sampling low or high ppb concentrations of H_2S.

Once the automated calibration sequence begins, the following events occur: (1) Sensor Regeneration ensures a gas free sensor at the beginning of calibration; the solenoid is not activated during this cycle so that only "clean" air passes over the sensor; (2) Linear Correction establishes a database of multipliers stored in the instrument's memory to correct for non-linearity; sampling continues until sensor saturation occurs; (3) Sensor Regeneration thermally desorbs all H_2S accumulated on the sensor during this portion of the calibration program; and, (4) Comparison Measurement compares the values measured by the instrument to the calibration gas. The correction factors are applied to maintain linearity.

TABLE 1

The instrument is calibrated with a Metronics Dynacalibrator using hydrogen sulfide permeation tubes. In this particular calibration sequence the calibration gas had been adjusted to 50 ppb, shown as the actual value below. The instrument's response to the gas is shown under the current value and its value is compared to the actual. Once the sensor has reached saturation (sample #69), a summary of the data, i.e. maximum and minimum values, average error, relative standard deviation, is calculated and printed.

```
        AUTOMATED CALIBRATION SEQUENCE
   Date = 04/24/85  *  Time = 14:12:59
   Instrument Serial Number: PPBH7
   Flow Rate = 150 CC's/minute
    Sample  Actual  Current  %Error
       1      50       51     +2.0
       2      50       51     +2.0
       3      50       51     +2.0
       4      50       50     +0.0
       5      50       50     +0.0
       6      50       49     -2.0
    ...
      31      50       49     -2.0
      32      50       50     +0.0
      33      50       50     +0.0
      34      50       50     +0.0
      35      50       50     +0.0
      36      50       50     +0.0
      37      50       49     -2.0
      38      50       50     +0.0
      39      50       50     +0.0
      40      50       50     +0.0
    ...
      59      50       50     +0.0
      60      50       50     +0.0
      61      50       50     +0.0
      62      50       50     +0.0
      63      50       50     +0.0
      64      50       50     +0.0
      65      50       51     +2.0
      66      50       49     -2.0
      67      50       50     +0.0
      68      50       50     +0.0
      69      50       49     -2.0
    Maximum value = 51
    Minimum value = 49
       Mean value = 50
    Average error % = -0.4
    Std. Dev. of Current Values = 0.6
    % Relative Std. Dev. of Current Values = 1.19
```

Single point calibration is sufficient to ensure linear responses through the range of the Hydrogen Sulfide Analyzer, 1 ppb to 500 ppb. An instrument calibrated at 50 ppb was operated in hydrogen sulfide gas streams where the concentration was changed from 275 ppb to 97 ppb to 58 ppb. The results are shown in Table 2. When the calibration gas was adjusted, it took several samples for the Hydrogen Sulfide Analyzer's readings to stabilize; this is to be expected. Note that the response of the Gold Film sensor was not affected by the other gases (CO, NO, and CO_2) in the gas cylinder.

TABLE 2

CASE STUDY: GOLD FILM PPB HYDROGEN SULFIDE ANALYZER COMPARISON MEASUREMENT OF KNOWN CONCENTRATIONS OF H_2S

The following data was obtained at a calibration laboratory for a state environmental monitoring program. The hydrogen sulfide calibration system included a Scott-Marin gas cylinder with 43ppm H_2S. Dilution was controlled using a Dasibi Mass Flow Controller. Sampling was done by connecting the PPB directly to the calibration gas. No effects were noted due to any positive pressure the calibration gas stream may have had. The calibration gas, in addition to H_2S, was made up of the following:

CO - 4990ppm
NO - 50ppm
SO_2 - 51ppm

No interference effects resulting from these other gases were noted.

SAMPLE	CAL GAS	PPB READING
1	275	250
2	"	261
3	"	267
4	"	271
5	"	270
6	"	268
7	"	268
8	"	269
9	97	191
10	"	116
11	"	100
12	"	97
13	"	98
14	"	98
15	58	81
16	"	57
17	"	56
18	"	58
19	"	57

Regarding other gases, the Gold Film sensor does not respond to aromatic hydrocarbons or water vapor. The sensor will respond to other reduced sulfurs.

The next set of test results were part of a test conducted by the Denver Research Institute. The Gold Film sensor was used as the detector for a gas chromatograph. Equal concentrations of a number of reduced sulfurs were analyzed with responses shown as compared with hydrogen sulfide.

TABLE 3

SUMMARY FOR ALL REDUCED SULFURS TESTED

(In order to normalize all these values, the ml/ppm was divided into the scale reading to give a value equal to 1 ppm.)

GAS 1 PPM	SCALE READING FOR 1 PPM	
H_2S - Hydrogen Sulfide	250	
ETSH - Ethyl Mercaptan	82	*
TBM - T Butyl Mercaptan	85	*
NPM - N Propyl Mercaptan	88	*
IPM - Isopropyl Mercaptan	85	*
SBM - Secondary Butyl Mercaptan	70	*
Methyl Mercaptan	80	* (done with permeation tube)
Dimethyl Disulfide	133	*
MES - Methyl Ethyl Sulfide	1.3	
DES - Diethyl Sulfide	2.9	
DMS - Dimethyl Sulfide	2.3	
Carbon Disulfide	1.5	(done with permeation tube)
TMT - Tetrahydro Thiophene	9.4	

* Prime Odorants

Research is now underway for the development of selective filters that would allow for quantification of a particular reduced sulfur group. Such an instrument could serve as a total reduced sulfur (TRS) analyzer especially as an odorant detector in the natural gas industry.

The Gold Film Hydrogen Sulfide Analyzer is now commercially available. It is the only instrument of its kind - portable, battery operated, yet able to directly determine hydrogen sulfide concentrations from 1 to 500 ppb. The operation of the instrument is simple: Instrument ON, Press SAMPLE, and in 10 seconds the results in ppb's are displayed on the digital readout.

The Gold Film Hydrogen Sulfide Analyzer may be operated as a fixed point, continuous monitor when interfaced with a desktop computer and Jerome Instrument Corporation's Single Point Continuous Monitoring Program. Sample interval is operator selectable from every 30 seconds to 1.5 hours. An alarm threshold value to alert personnel when hydrogen sulfide concentrations exceed a critical value can be programmed in. Periodic summaries of the data are also operator selectable.

Jerome Instrument Corporation has recently developed Dilution Modules which allow the Gold Film Hydrogen Sulfide Analyzer to sample ppm concentrations of H_2S. These small modules are inserted into the intake of the analyzer. Modules are available to expand the range of this instrument to 500 ppm H_2S.

THE STATE OF DELAWARE EXPERIENCE
WITH
EPA REFERENCE METHOD 25 AUDIT SAMPLES

CHARLES S. KRICK, P.E.
JOHN W. PERONTI
STATE OF DELAWARE
DEPARTMENT OF NATURAL RESOURCES
AND
ENVIRONMENTAL CONTROL

BACKGROUND

The State of Delaware routinely requires the analysis of audit samples when stationary sources are tested for gaseous pollutants. EPA liquid audit samples are required for SO_2 and NO_x, and EPA cylinder gases are utilized for non-criteria organic pollutants, as well as non-methane hydrocarbons.

We have required the use of EPA Reference Method 25 on four occasions. Two of the tests were at bulk gasoline terminals, and the other two were at an automobile assembly plant before and after a modification to the paint line.

BULK GALSOINE TERMINALS

The bulk gasoline terminal tests were performed by Scott Environmental Technology, Inc., and were accomplished one week apart. Accordingly, one audit gas was used for both tests.

The analytical equipment consisted of two infrared hydrocarbon analyzers: a LIRA Model 300 (0-1.4% propane range) and an Infrared Industries (0-70% propane range). The instruments were spanned with 1.2% and 52.4% propane in nitrogen respectively. 100% nitrogen was used to zero the instrument. Calibration curves were generated prior to the test for both the LIRA and the high and low ranges of the Infrated Industries analyzers.

The 9 point calibration curve for the LIRA Model 300 was non-linear. The five point calibration curve for the low range of the Infrared Industries analyzer was linear. And the seven point calibration curve for the high range of the Infrared Industries analyzer was linear.

The test methods used were Method 2A for the direct measurement of the gas volume. The volume meter had been factory calibrated and was checked using a standard pitot and wind tunnel. And Method 25B was used to determine the total gaseous organic concentration as propane.

The propane audit sample was obtained from the EPA and was supplied by the Research Triangle Institute. A sample was taken from the cylinder into a bag. The bag was then connected to the sample line and analyzed directly on the LIRA Model 300. The results were 90.5% of scale, which was 1.29% propane on the calibration curve. The audit gas which was propane in air had been analyzed in March, 1983, as 1.18% propane and, in May 1984, as 1.3% propane. The initial audit results were within 10% and were considered to be acceptable.

The results of the tests were considerably different. The weighted average for one test was 21.3 mg/l, and the other test was 5 mg/l.

In view of the test results and the analytical equipment which was used, the following conclusions can be reached:

1) The audit gas was analyzed within acceptable limits (10%).

2) For a non-linear detector, low and high range audit gases would have been more meaningful.

3) The results from different sources can vary widely. If the results can be predicted, audit gas concentrations can be obtained which would cover the range of concentrations to be expected.

4) The scope of the audit gas program is a function of the purpose of the testing program. The purpose of this test program was to establish compliance with a State Regulation. The audit gas used was approximately 50% of the average concentration for compliance. More than 90% of the concentrations were below the level of the audit gas. The 1.18% audit gas was appropriate for a compliance determination.

AUTOMOTIVE ASSEMBLY PLANT

The automotive assembly plant modified its existing topcoat operation to use the base coat/clear coat coating technology. This modification required two side-by-side spray booths. Then curing was achieved in the existing oven. The exhaust air system is vented through 14 stacks on each spray booth after water scrubbing for particulate removal. The oven exhaust is vented through 5 stacks. Because of the number of exhaust stacks, we chose to test 8 spray both stacks and an oven stack.

Method 5 testing for particulates and Method 25 for Volatile Organic Compounds were conducted. The following analytical equipment was used for the Method 25 testing:

- Byron Model 401 automated G.C. for analysis of total hydrocarbons, non-methane hydrocarbons, methane, carbon monoxide and carbon dioxide
- Byron Model 90 battery powered stack sampler
- Byron Model 75 digestion oven
- Beckman CO_2 analyzer (NDIR)
- Beckman Hydrocarbon Analyzer
- Servomex oxygen analyzer (paramagnetic)
- Metal bellows sampling pump

All instruments were calibrated with NBS traceable gases. Calibrations were accomplished before each analyses. The Model 90 and Model 75 each have digital mass flow meters which were calibrated against each other daily.

The Method 25 sampling was accomplished using the Byron Model 90 which pumps the sample through an adsorption tube and into a Tedlar Bag. The sampling is accomplished at the stack. There were 3 to 4 liters per run. The run times were 15 to 20 minutes in length.

There was a direct sample line which was used to continuously monitor for CO_2, O_2, and total hydrocarbons.

The bags from the Model 90 were analyzed directly on the Model 401. The adsorbent tube was purged with zero air to remove any CO_2 or CO into a second bag. The second bag was analyzed on the 401 for any VOC's removed from the tube during the purge. The adsorbent tube was then heated in the Model 75 oven to convert the remaining organic compounds to CO_2 which were then collected in a third bag. The third bag was then analyzed for CO_2. The total non-methane hydrocarbon content of the sample was calculated as ppm carbon as the sum of the NMHC in the first two bags plus the CO_2 in the third bag.

EPA Reference Method 25 audit gases were obtained for both the March and the June/July test series. There were two gases for each series. None of the audit gases were analyzed satisfactorily. But there was a marked improvement for the second set. The results are summarized below.

	Component	Company	EPA	% Difference
March	CO_2 (%)	3.4	5	-30
	Total NMHC (ppm C)	194	107	+80
	CO_2 (%)	3.5	5	-30
	Total NMHC (ppmC)	1081	775	+40
June/July	CO_2 (%)	4.7	5	-5
	Total NMHC (ppm C)	249	205	+21
	CO_2 (%)	3.9	5	-20
	Total NMHC (ppm C)	1240	1043	+19

The company consistently underestimated the CO_2 level while overestimating the non-methane hydrocarbons. In conversations with Dr. Jayanty of RTI, he indicated that the company's values for the NMHC of the digest portion appeared to be high. This suggests that all the CO_2 was not being removed from the adsorption tube, and ended up as being considered NMHC. This is supported by the improved analysis of the audit gases for the June/July test series. The March test series and audit gas analysis had equal 4 liter volumes for the sample, purge, and digest. The June/July test series had sample volumes of 3.4 liters, purge volumes of 5.1 liters and digest volumes of 1.7 liters. It appears that the increased purge volume resolved some of the problem with the audit gas analyses.

The CO_2 values in the stacks which were tested did not appear to be high enough to affect the results. While the change in the ratio of the sample, purge, and digest volumes could have affected the results, such changes were not readily apparent.

The conclusions regarding the use of the audit gases at the automobile assembly plant are that:

1) The audit gases were not analyzed satisfactorily.

2) The audit gases were not representative of the sample gases (5% CO_2 vs. 0.04 - 1.5% CO_2). This decreased the significance of the audit gas analytical error.

3) The change in methodology improved the audit gas analytical results, but made the interpretation of the before and after results more difficult.

CONCLUSIONS

1. If possible, the use of two audit gases is desireable. One audit gas should represent the compliance level, and one should represent the expected range of emissions. The expected range of emissions is not that easy to determine as shown by difference between the two bulk gasoline terminals.
2. The results of the audit gas analysis should be interpreted. If there is a question regarding the analysis which could effect the validity of the tests, RTI should be requested to reanalyze the gas. The bulk gasoline audit gas analysis varied from 1.18% to 1.3%. Also, the suitability of the audit gas for the particular test should be a consideration when interperting the results. The automobile assembly plant did not have the CO_2 levels which were in the audit gas, thus reducing the significance of the variance.

UTILIZATION OF EPA METHOD 25 FOR THE MEASUREMENT OF VOLATILE ORGANIC CARBON (VOC) EMISSIONS FROM COMBUSTION AND STEAM SOURCES

G.C. Simon, National Council for Air and Stream Improvement

ABSTRACT

A series of simple modifications to the method allows accurate testing of combustion gases from industrial boilers without significant interference from carbon dioxide. Similarly, another set of minor modifications makes the sampling of steam vents possible without trap or catalyst overloads.

The hardware alterations and procedural changes will be fully described. Data from thirteen wood-residue fired power boilers will be presented, including data from three units that were tested concurrently using either a flame ionization detector or infrared spectrometer in the field. Data from several thermomechanical pulping operations will also be presented.

I INTRODUCTION

Volatile organic compounds (non-methane hydrocarbons) participate in photochemical reactions which lead to formation of ozone in the ambient atmosphere. Ozone has been designated as a criteria pollutant by the U. S. Environmental Protection Agency, and ambient air quality standards have been set to protect against adverse health and welfare effects. To control the formation of ambient ozone, EPA has emphasized the control of volatile organic compound (VOC) emissions from both mobile and stationary sources. EPA considers only methane, ethane, methyl chloroform, methylene chloride and certain fluorocarbons and chlorofluorocarbons to have negligible reactivity, and thus not be categorized as VOCs (1). VOC emissions from many types of new stationary sources, e.g. paper coating facilities, are limited by New Source Performance Standards. In addition, obtaining construction permits for new sources or for modifications to existing sources often involves estimating VOC emission rates to determine what types of permitting requirements and emission control considerations apply.

Accurate VOC emission estimates are important in obtaining permits for new or modified sources located in both ozone nonattainment areas as well as attainment areas. In nonattainment areas, VOC emissions from a new source must be offset by VOC emission reductions from other existing sources in the area. Permit applicants in ozone nonattainment areas must also demonstrate that their VOC emissions represent the lowest achievable emission rate. In attainment areas, permit applicants must show that best available control technology (BACT) will be used to control VOC emissions from new or modified sources. However, this BACT review need not be conducted if there is no significant net increase in VOC emissions resulting from the project, and possible ambient ozone monitoring and modeling requirements can also be avoided.

In the past few years, the National Council staff has received numerous inquiries concerning VOC emissions from various forest products industry sources. Most of these inquiries have been in connection with obtaining permits for new or modified sources. A particularly interesting situation involving installation of a new wood-fired boiler at a mill near a metropolitan ozone nonattainment area was recently described (2). The mill was required by the permitting agency to obtain VOC emissions offsets for the new boiler, and VOC emission factors for the new boiler proved to be an extremely important issue in the permitting process. Similar situations have occurred in many other permitting circumstances.

In an effort to provide the industry with reliable VOC emission data, the National Council has been surveying major sources at forest product manufacturing facilities in the United States utilizing EPA Method 25. To date, VOC emission measurements have been reported on kraft recovery furnaces, lime kilns, wood residue fired power boilers in the Northwest and Southeast, veneer dryers and thermomechanical pulping (TMP) operations (3,4,5,6,7,8). Modifications to the basic method were necessary to overcome CO_2 interference problems associated with combustion source samples and high moisture levels (>90%) associated with TMP samples. These modifications are presented in detail in the following sections.

In addition, during the course of these studies three opportunities arose for the National Council staff to sample combustion sources using the modified EPA Method 25 concurrently with contractors or mill personnel using alternate techniques. In two instances a flame ionization detector was used on-site, and in a third test the contractor employed an infrared spectrometer on-site. Results from these comparative tests are also presented.

II METHOD 25 MODIFICATIONS

For details of Method 25, readers should refer to the *Federal Register* (45 [194] October 3, 1980). Only the modifications, and reasons for them, are described below.

A. Sampling Equipment and Procedures

(1) Trap Design - To allow condensation of several milliliters of water without trap plugging, the trap was enlarged to 1 inch O.D. by 7.5 inches long and filled with fine quartz wool instead

of stainless steel turnings. The trap body was low carbon 316 stainless steel and the inlet/outlet tubes, the 4 ft. x 1/8 in. probe, and the fittings were standard 316 stainless steel (Figure 1). It was felt that the firmly packed fine quartz wool would be more efficient in retaining aerosols formed in the trap during the condensation process. In addition, three No. 40 holes were bored through the exit tube instead of one. This allowed gas flow to continue even after more then 20 mL of water had been collected.

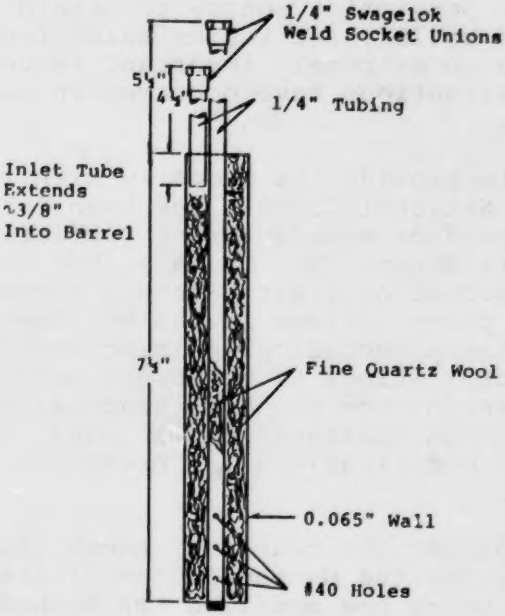

1/4" Swagelok Weld Socket Unions
5½"
4½"
1/4" Tubing
Inlet Tube Extends ~3/8" Into Barrel
7½"
Fine Quartz Wool
0.065" Wall
#40 Holes

FIGURE 1 NCASI METHOD 25 TRAP DESIGN

(2) Flow Controller Design - Specifications only require a flow control system that is "capable of maintaining the sampling rate within ±10% of the selected flow rate (50 to 100 mL/min)" (10). Flow controllers used in our work consisted of all glass/Teflon rotameters (Gilmont, 0 to 200 mL/min) connected via a thick walled 1/8 in. Teflon tube to a pressure/vacuum gauge-metering valve-quick connect assembly. All assembly components and fittings (Swagelok) were stainless steel.

(3) Sample Tanks - Six-liter cylindrical stainless steel sampling cylinders were used for sampling tanks (Daytron Systems, Nicholson Division, Wilkes-Barre, PA). These tanks were thoroughly cleaned, their volumes measured, and then equipped with stainless steel quick connects on one end and plugs on the other end.

(4) Particulate Filters - Filter assemblies were constructed from 4 in. long x 1/2 in. diameter stainless steel tubes that were firmly packed with clean borosilicate glass wool and fitted with 1/2 in. to 1/4 in. stainless steel Swagelok reducing unions. A 1/4 in. tube stud to 1/8 in. Swagelok stainless steel reducing union, also packed firmly with Pyrex wool, was used to couple the large filter to the trap probe line. This entire assembly was wrapped with several layers of aluminum foil to keep soot (boiler/samples) or tar (TMP samples) off of the fittings, thus minimizing contamination during disassembly. Any visible breakthrough of particulate matter onto the 1/4 in. tube stud filter was indicative of contamination and grounds for data rejection. In practice, this rarely occurred. Filters were placed in the flue gas facing generally downstream to avoid particle impingement and positioned appropriately to avoid collection of condensate from post-scrubber aerosols or liquified tars that impinged on the probes' and filter assemblies' outer surfaces.

(5) Pre-sampling Leak Check Procedure - Sample traps, with the probe tips plugged, and flow controllers were assembled and then pressurized to 25 psi with nitrogen and isolated. The pressure was observed for 5 to 10 minutes while trap fittings were wetted with a bead of distilled water and inspected for leaks. Flow controller fittings were wetted with Snoop and checked for leaks before being rinsed thoroughly with distilled water. Leaks were either repaired on the spot or the sample train component was replaced. A pressure drop of less than 1 psi after 5 minutes was acceptable. This pressurized leak check allowed the use of "leaky" equipment by providing a means of isolating and repairing the leak without contaminating the component. After the leak check, the pressure was released, the filter tips and evacuated sampling tanks connected, and the filter assemblies placed several feet into the stack facing downstream as described above.

(6) Sample Collection Procedure - Replicate boiler samples were drawn at a nominal flow rate of 80 mL/min. The flow was controlled by observing the rotameter and adjusting the metering valve to compensate for the changing vacuum force in the sample tank. A trap freeze-up, as evidenced by a very low flow rate, was dealt with by gently warming the top of the trap near the inlet tube with a propane torch until a normal flow was re-established.

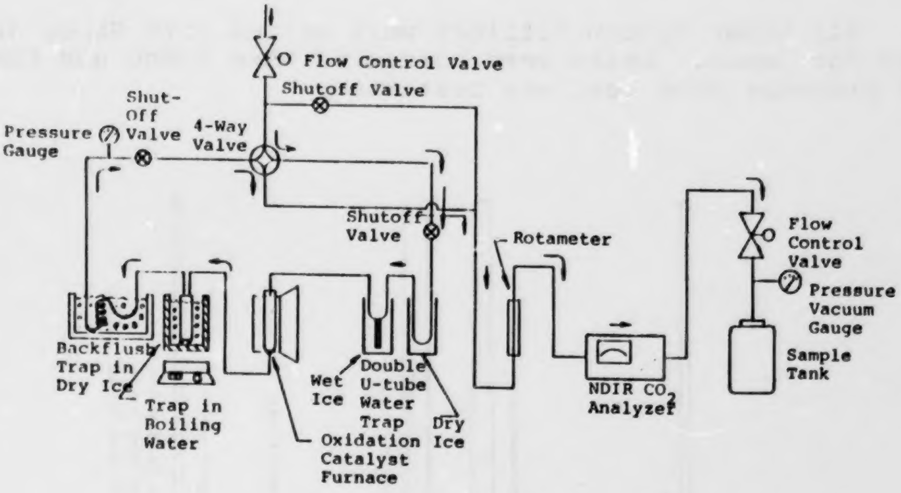
The NCASI trap design also allowed the collection of steam samples from TMP vents which tended to fill the traps with water. Because the dry gas content was so low (1 to 10% by volume) in these sources, the flow rate into the evacuated tank was extremely low (<10 mL/min). However, the flow rate of water vapor into the trap was 10 to 100 times greater. A qualitative technique was developed in the field to judge the moisture flow rate into the trap. Steam entering the 4 ft. x 1/8 in. sampling probe condensed to a liquid as it cooled to near ambient temperature. The rapid temperature drop at the condensation point along the probe length could be physically detected by touch. The dry gas flow rate was adjusted until the steam condensation point was 6 to 12 in. from the stack wall. This technique resulted in the collection of 20 to 30 mL of liquid in ca. 30 min. Steam samples were also collected in replicate.

(7) Post Sampling Leak Check Procedure - After closing the metering valves and removing the filter/probe assemblies from the stack, the probe tips were again plugged. The metering valves were opened and the trap/flow controller assembles were evacuated to the level of the respective sample tank's vacuum. The metering valves were then closed and the vacuum gauge readings were observed for ten minutes. A change of less than one inch of mercury vacuum was acceptable. Larger leaks were noted and dry gas concentrations in the replicate sample tanks were compared to evaluate the extent of the leak. In practice, leaks were rarely found after sampling. A relative standard deviation greater than five percent between duplicate sample dry gas concentrations was grounds for data correction or rejection.

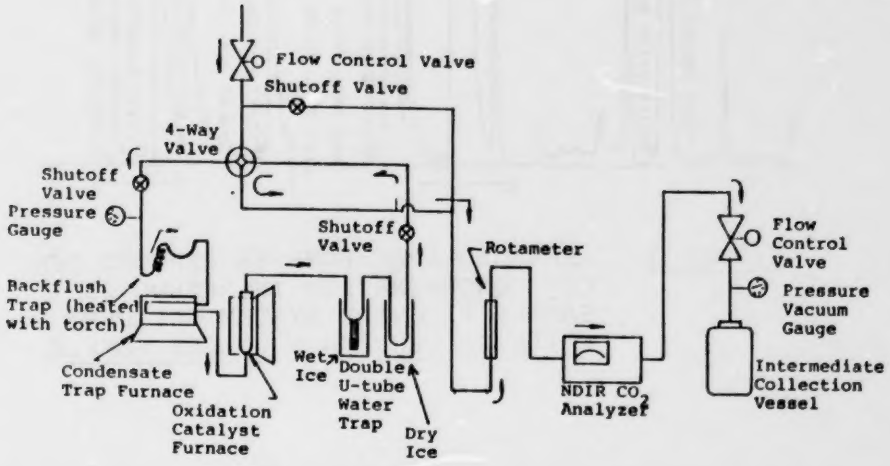
B. Analysis Equipment and Procedures

(1) Condensate Sample Recovery System Modifications - Sample trap probes were hooked directly to the recovery system's oxidation catalyst and sequentially heated along with the trap and backflush condensers to 600°C all the way up to the catalyst hot zone using a tube furnace and a MAPP gas torch. The zero air carrier gas flow rate was 100 to 150 mL/min. The catalyst tube was a 14 in. long by 1 in. O.D. low carbon 316 stainless steel tube packed with 10 inches of small grain manganese dioxide. It was heated to 700°C by a Lindberg tube furnace in the vertical position (Figure 2). This minimized channelling due to catalyst settling. This catalyst was found very efficient at oxidizing high levels of organics (i.e. 200 mg C/sampling), and resistant to sulfur poisoning. Catalyst efficiencies remained >98% even after a year or longer.

Both the backflush gases and the sample recovery gases (the catalyst effluent) passed through an IR (Beckman Model 864) before entering the appropriate collection vessels. The IR monitor was used in the 0 to 100 ppm range for boiler samples, and 0 to 1.5 percent for highly loaded steam samples to determine when all of the CO_2 had been removed from the system during each cycle. Even though the baseline tended to drift with the changing pressure on the system as the tanks were filled, the trap effluent could be stopped and zero air fed directly into the IR via a system bypass loop to re-establish the baseline level at the higher pressure. Using this technique, very low levels (less than 5 ppm) of CO_2 could be accurately observed (Figure 3). A dry ice/water cooled double glass U-tube condensed and collected the water in the sample trap for subsequent quantitation. The first of these tubes was fitted with a reservoir made from a buret and sealed to the bottom of the U.


Flow Control Valve
Shutoff Valve
Shut-Off Valve
4-Way Valve
Pressure Gauge
Shutoff Valve
Rotameter
Flow Control Valve
Pressure Vacuum Gauge
Sample Tank
Backflush Trap in Dry Ice
Trap in Boiling Water
Wet Ice
Double U-tube Water Trap
Dry Ice
Oxidation Catalyst Furnace
NDIR CO_2 Analyzer

Backflush Mode


Flow Control Valve
Shutoff Valve
4-Way Valve
Shutoff Valve
Pressure Gauge
Shutoff Valve
Rotameter
Flow Control Valve
Pressure Vacuum Gauge
Backflush Trap (heated with torch)
Condensate Trap Furnace
Oxidation Catalyst Furnace
Wet Ice
Double U-tube Water Trap
Dry Ice
NDIR CO_2 Analyzer
Intermediate Collection Vessel

Burn Mode

FIGURE 2 CONDENSATE SAMPLE RECOVERY SYSTEM

(2) Recovery System Leak Check Procedures - Recovery system leak checks were performed by pressurizing the entire system with zero air to 20 psi with the sample trap in place in the backflush mode. After waiting several minutes for the pressure to equilibrate (the heat input from the catalyst caused some slight pressure increase in the closed system for the first 1 to 2 minutes), the pressure was recorded and then rechecked 10 minutes later. A drop of less than one psi was considered acceptable. During the ten minute waiting period all trap fittings were wetted with a bead of distilled water and observed for signs of

leaks. All other system fittings were wetted with Snoop and checked for leaks. Leaks were corrected when found and the 10 minute pressure drop test was restarted.

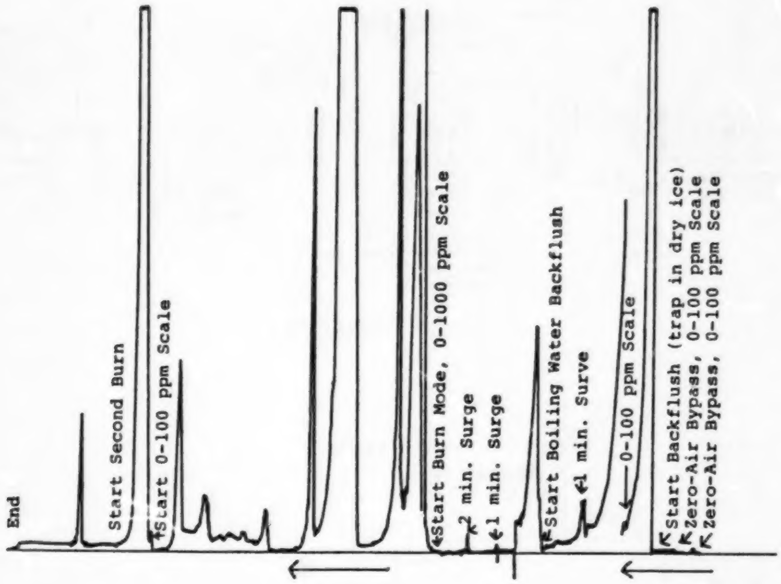


FIGURE 3 INFRARED SPECTROMETER READOUT OF CO_2 CONCENTRATION IN METHOD 25 SAMPLE RECOVERY SYSTEM EFFLUENT WHILE PROCESSING A BOILER SAMPLE

(3) Backflush and Sample Recovery Procedures - Boiler sample traps were subjected to a "warm purge" during the backflush cycle. The gases in the sample trap were flushed into the sample tank using zero grade air. In combustion source samples, the presence of high concentrations of water vapor and carbon dioxide causes some potential interference to hydrocarbon recovery. This is caused by CO_2 dissolving in the water in the sample trap during cooling and subsequent entrapment in the water-ice matrix on freezing. To eliminate this potential positive bias, the traps were placed in boiling water and vibrated sharply during the backflush cycle. This action effectively drove off the entrapped CO_2, while vaporizing very little water (Figure 3). The backflush gases were passed through a dry ice condenser consisting of a 9 in. long by 3/8 in. O.D. stainless steel tube packed with quartz wool and immersed in dry ice. This condenser was backed up with a secondary dry ice cooled condenser constructed from three feet of coiled 1/8 in. stainless steel tubing. These condensers caught any condensible hydrocarbons

that vaporized during the warm purge and were sequentially heated to 600°C along with the trap and probe during the recovery procedure, using zero air for carrier gas (Figure 2). Traps were heated quickly since generally organic loadings were <1 mg as Carbon, and water contents were <3 mL. These levels represented light loadings to our large catalyst. Steam sample traps were subjected to the standard dry-ice temperature backflush, and then warmed in a boiling water bath to drive off most of the organics with very little water. Auxiliary oxygen was added at 50 to 150 mL/min. just before the catalyst when effluent CO_2 concentrations were >1.0% . When the bulk of the organics were out, the trap was heated slowly with a torch while the system pressure was monitored. Both backup condensers in the recovery system were still immersed in dry ice in order to prevent any moisture and organics from contaminating the system in case of pressure surges due to the water vaporization. The high volumes of water (20 to 30 mL/sample) tended to cool the catalyst if put through too quickly. Recoveries of steam samples typically took three hours. All intermediate collection vessels were analyzed for combustion by-products to assure efficient recoveries.

Due to the modified design of our Method 25 traps, there were many "dead spaces" where gas flow was restricted. In order to assure that these spaces were swept clear of CO_2, a "surge" technique was used. This technique involved stopping the air flow through the trap for one minute to allow diffusion of CO_2 from dead spaces. The flow was then restarted and a CO_2 peak was observed on the IR. For low level samples, when the peak caused by a surge was less than 5 ppm, and the background CO_2 concentration was less than 2 ppm, the system was considered cleared (Figure 3).

After completion of the sample recovery, the trap was removed from the tube furnace and allowed to cool in the ambient air for about five minutes before being sealed. Eventually this technique was changed, and the hot traps were placed in a bucket of dry ice and allowed to cool down to -75°C while zero air was flowing through before being sealed and stored at ambient conditions until used. This technique caused the trap to be stored under positive rather than negative pressure (trap sealed while hot). This caused a significant improvement in blank levels during the course of these studies (Table 1), presumably due to a reduction in contaminate infusion which occurred when the trap seals were broken. Although blank levels improved with investigator experience, it was not until the institution of the cold sealing technique that consistently low blank values were achieved. This technique was used for low level samples only.

(4) Sample Analyses - A non-methane organic (NMO) analyzer from Byron Instruments, Raleigh, NC (Model 401S) was used throughout this study for gas analyses. This unit was capable of separating non-methane hydrocarbons, methane, carbon monoxide, and carbon dioxide and passing each component individually through an oxidation catalyst for conversion to CO_2, and then through a

reduction catalyst for conversion to methane and subsequent quantitation on a flame ionization detector. All of these actions occurred automatically once the analysis cycle was begun. This system differed in several respects from the system recommended by EPA Method 25. The same separations and measurements were achieved, but the physical arrangement of the hardware and the column packing materials were altered.

TABLE 1 METHOD 25 BLANK VALUES

DATE	TRAPS SEALED HOT OR COLD	RESULTS Micrograms Carbon	RESULTS As ppm in a 5 Liter Sample
April, 1982	Hot	177	71
		167	67
		168	67
	Average	171	69
October, 1982	Hot	115	46
		48	19
		85	34
	Average	83	33
February, 1983	Hot	42	17
		28	11
	Average	35	14
March, 1983	Hot	66	27
		87	35
		38	15
	Average	64	26
April, 1983	Cold	20	8
		25	10
		15	6
	Average	20	8

III LABORATORY CO_2 ABSORPTION INTERFERENCE STUDY

Most combustion sources have stack moisture contents above 20% and carbon dioxide concentrations above 10%. At these conditions the interference from CO_2 absorption in the water-ice matrix can be significant.

Adsorption characteristics of carbon dioxide in the cryogenic traps used in these studies were determined in the laboratory using several different sample stream carbon dioxide and moisture concentrations. The test covered conditions of no CO_2 or moisture to 18% CO_2 and 50% moisture in the gas stream. Results from the tests are reported in a format that allowed correction of field sample data for the interfering CO_2.

(1) Procedure - Carbon dioxide in air mixtures were directed to a heated U-tube containing water to add moisture to the air stream. The water added to the U-tube was passed through activated carbon to remove organics. The quantity of moisture added to the air stream was roughly controlled by adjusting the temperature of the U-tube. This moisturized air was passed through a MnO_2 oxidation catalyst at 600°C to insure that there were no organics delivered to the trap. After the oxidation catalyst the gas passed through a cryogenic trap set in dry ice, to a flow meter and to a 17-liter evacuated tank. This apparatus is the trap burnout system used in reverse but with a sample collected as in the field. Gas flow was controlled to 200 cc/min until 10 liters of gas were collected.

The trap was then flushed with carbon dioxide free air flowing at 100 cc/min until the NDIR registered less than 10 ppm CO_2. Flushing of the traps took from 20 min. to 1 hr.

After flushing, the trap was heated with an acetylene torch with the CO_2-free sweep-gas passing through the oxidation furnace, a cold trap to remove moisture, the NDIR detector, and into an evacuated collection vessel. When all of the CO_2 was removed from the trap, as indicated by the NDIR, the collection vessel contents were analyzed. The amount of water collected in the cold trap was used to determine the gas stream moisture content.

(2) Results - Results of the carbon dioxide interference study are shown in Figures 4 and 5. Figure 4 shows a constant background carbon dioxide interference for all moisture levels when the sampled gas contained less than 5 ppm CO_2 or 659 ppm CO_2. After elimination of one data point from the 650 ppm CO_2 data, the log average CO_2 background was 8.0 ppm CO_2 for the 659 ppm CO_2 data, and 8.1 ppm for the 0% CO_2 data. The log average of all the data when no moisture was added to the traps was 7.4 ppm. These results show that when there is no water present in the trap, all of the carbon dioxide is successfully removed from the trap during flushing.

Figure 5 shows the CO_2 absorption interference as a function of sampled gas moisture content at carbon dioxide concentrations between 8 to 18%. Below 20% moisture there appears to be no significant interference above background. Above 20% flue moisture there appears to be a random interference that increases with sampled gas moisture and carbon dioxide content. The randomness of this data makes it difficult to predict the CO_2 interference encountered at high stack moistures. Figure 6 shows the same data in terms of mL H_2O caught in the trap.

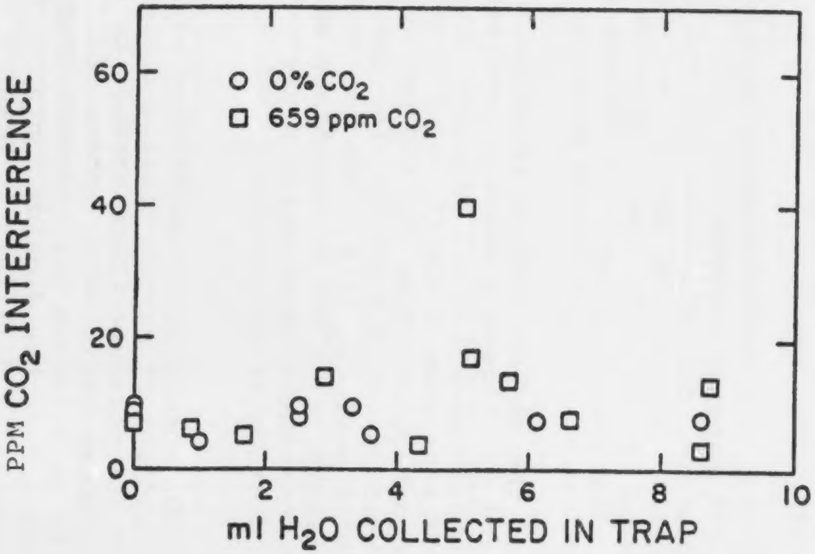


FIGURE 4

CO_2 INTERFERENCE AT LOW STACK GAS CARBON DIOXIDE CONCENTRATIONS

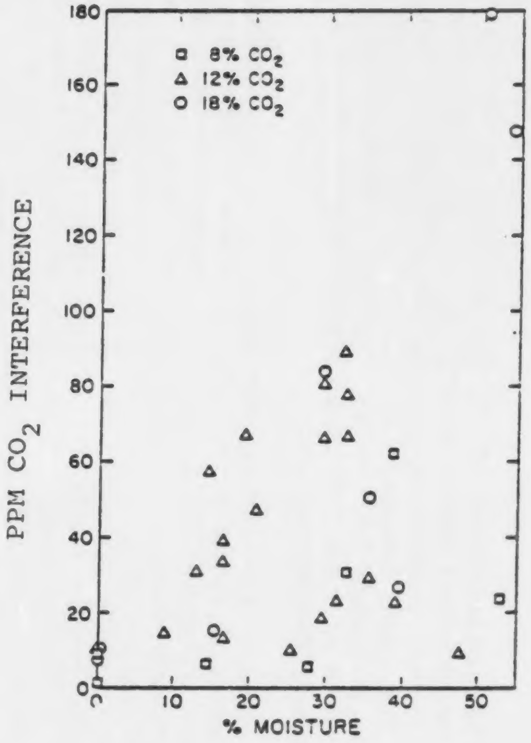


FIGURE 5

INTERFERENCE AT HIGH STACK GAS CO_2 CONCENTRATIONS AS A FUNCTION OF STACK GAS % MOISTURES

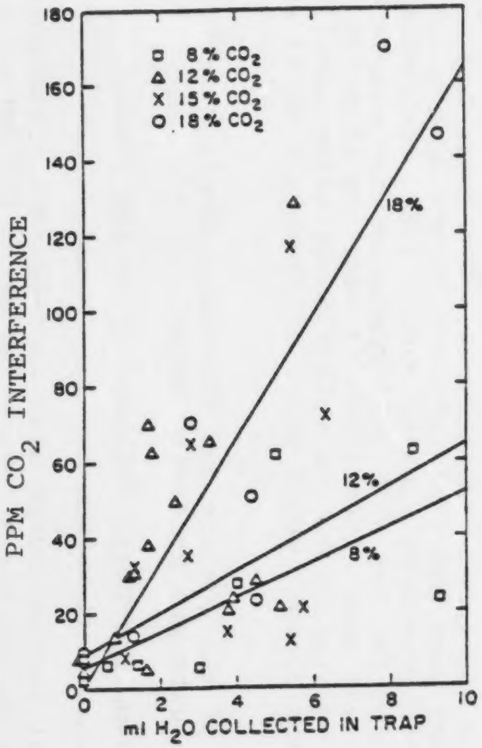


FIGURE 6

INTERFERENCE AT HIGH STACK GAS CO_2 CONCENTRATIONS AS A FUNCTION OF WATER COLLECTED IN SAMPLING TRAP

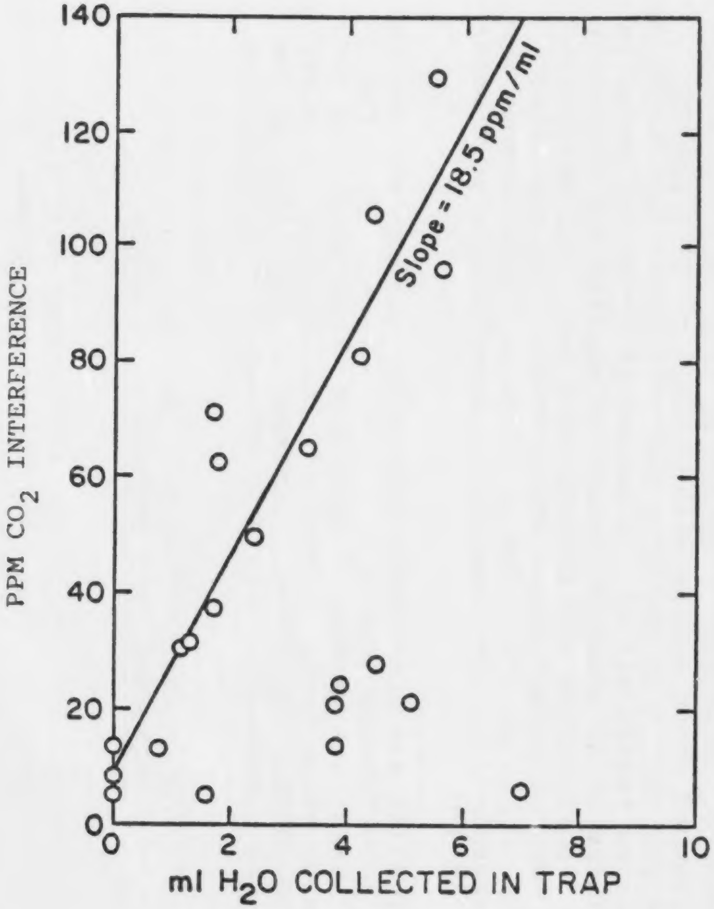


FIGURE 7

CARBON DIOXIDE INTERFERENCE AT 12% CO_2 IN STACK GAS

A closer look at all the data collected for 12% CO_2 (Figure 7) shows that the CO_2 interference tended to fall into two groups, that which grouped about a line with a slope of 18.5 ppm CO_2 interference per mL H_2O in the trap and that which fell below 30 ppm interference regardless of the amount of water collected in the trap. There is no apparent reason to explain the different groupings. Almost all of the interference data fell below the theoretical maximum interference which occurs when the water absorbing the CO_2 is at 0°C. The 18.5 ppm CO_2 interference per mL water corresponds to the theoretical interference at a water temperature of 3°C.

These results are consistent with other workers who reported erratic CO_2 interference levels in a similar study (9). The "warm purge" backflush technique described above minimized this interference by effectively driving off the CO_2 from the water by heating it to 100°C. The dry-ice immersed backup traps in the recovery system prevented any loss of condensible hydrocarbons.

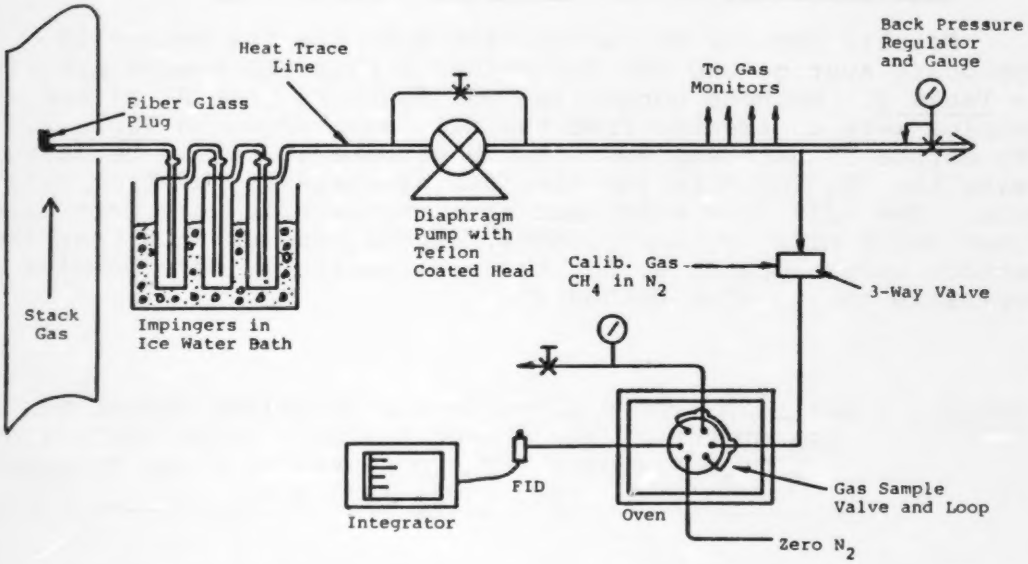
IV EVALUATION OF ALTERNATIVE METHODS FOR MEASURING VOC EMISSIONS FROM INDUSTRIAL BOILERS

In an effort to identify potentially useful equivalent alternative techniques for measuring boiler VOC emissions, three simultaneous sampling tests were performed with either private contractors or mill personnel. The three tests were on emissions from a Dutch oven wood-residue fired boiler, a bagasse fired boiler, and a combination wood fines and natural gas fired boiler. In each test, NCASI staff sampled the flue gases with EPA Method 25 as described earlier, while the other groups used (a) an EPA Method 5 particulate train followed by a flame ionization detector (FID), (b) a Byron Model 4015 hydrocarbon analyzer, and (c) an infrared analyzer, respectively. The first two alternate techniques were modified versions of EPA Method 25A, while the third technique approximated Method 25B. Both of these methods were intended for use with well characterized sample streams, but there was some expectation of adapting them for flue gas sampling. An equivalent method utilizing existing sampling equipment with minor changes would offer an advantage to affected facilities.

Descriptions of the boilers and alternate sampling techniques and comparative results are presented below.

A. Particulate Sampling Train Followed by an FID Versus Method 25

Mill personnel sampled Dutch oven wood-residue fired boilers for VOCs using a sampling train consisting of an EPA Method 5 particulate sampling train followed by an FID, as shown in Figure 8. The sampling nozzle was turned upstream in the stack to minimize particulate capture. Particles entering the probe were filtered by stuffing the probe with glass fiber. No filter was used in the sampling train oven. The sample was cooled and water removed with three impingers in an ice water bath. Sampling started with 100 mL water in each of the first two impingers and the third impinger dry. A Teflon coated diaphragm pump drew the sample gases through a heat traced Teflon line into a sampling manifold in a trailer.



Heat Trace Line
Fiber Glass Plug
To Gas Monitors
Back Pressure Regulator and Gauge
Stack Gas
Impingers in Ice Water Bath
Diaphragm Pump with Teflon Coated Head
Calib. Gas CH_4 in N_2
3-Way Valve
Integrator
FID
Oven
Gas Sample Valve and Loop
Zero N_2

FIGURE 8 EPA METHOD 5 PLUS FID SAMPLING TRAIN

Samples were delivered to an FID via a 0.1 mL sample loop every two minutes in a nitrogen carrier gas. The gas pressures in the sampling loop and the sample loop temperature (100°C) were kept constant so that an equal volume of sample was delivered to the FID. The FID was calibrated with methane in nitrogen via the sample loop.

A small sampling loop size was used to dilute the sample enough so that changes in FID response due to CO_2 and moisture in the sample would be avoided. A 1/16 in. stainless steel tube led from the valve to the FID. The GC oven and manifold were at 120°C and 200°C, respectively.

Organics that condensed in impingers were analyzed by a TOC (total organic carbon) analysis of the impinger water and drying and weighing an acetone rinse of the EPA Method 5 train probe and glassware. Impinger water TOCs were used instead of ether extraction and drying, as recommended for EPA Method 5 back half analysis, because of possible volatile organic material losses during drying. Comparison of analysis by weight to the TOC analyses showed the drying and extraction result to be consistently much less than the TOC result. The sums of the TOC and the dried acetone rinse weights of the EPA Method 5 train analysis were added to the FID response to give a total gaseous organic carbon result.

B. Results of Method 5 Plus FID Versus Method 25

Results for VOC emissions from both the EPA Method 25 duplicate average and the EPA Method 5 plus FID trains are listed in Table 2. Methane concentrations found in the EPA Method 25 samples were subtracted from the mill data shown in Table 2. The EPA Method 25 data expressed as lb methane/10^6 Btu were calculated using the CO_2 found in the tank during analysis and from mill O_2 data. The mill data expressed as lb methane/10^6 Btu were calculated using mill CO_2 and O_2 data. These results show that the methods were comparable, but the alternative is more complex and expensive to run than Method 25.

TABLE 2 BOILER G - COMPARISON OF VOC EMISSIONS DETERMINED BY EPA METHOD 25 AND METHOD 5 PLUS A FLAME IONIZATION DETECTOR (DUTCH OVEN WOOD-RESIDUE FIRED BOILER) TEST DATES 12/3-4/80

	NCASI-EPA METHOD 25 VOC (as methane)			MILL-EPA METHOD 5 PLUS FID VOC (as methane)		
MILL TEST NO.	ppm	lb/10^6 Btu From CO_2	lb/10^6 Btu From O_2	ppm	lb/10^6 Btu From CO_2	lb/10^6 Btu From O_2
2	380	0.44	0.43	363	0.37	0.42
3	278*	0.39	0.29	387	0.34	0.40
5	341	0.32	0.33	355	0.31	0.34

---

*This sample had a leak.

C. Hydrocarbon Analyzer Field Technique Versus Method 25

A Byron 401S analyzer was housed in a small trailer on-site at the base of a bagasse fired boiler stack. About 250 feet of heat traced Teflon line was used to transport the sample from a stainless steel in-stack filter holder fitted with a glass fiber filter. The sample line was kept at 250°F; the stack temperature was 155°F. The analyzer was operated in the "full cycle without CO_2" mode, which gave results for a direct FID injection, non-methane hydrocarbons, methane, and carbon monoxide. About two liters per minute of sample gas were drawn from the stack with a Teflon diaphragm pump to a splitter. Thirty mL/min were pulled through the analyzer's sample loop with a second pump. All lines and connections were wrapped with heat tape up the entrance to the 401S. This left about eight inches of unheated 1/8 inch diameter stainless steel line that was warmed to about 160°F by the instrument's heat. The sample then entered the sample loop which was maintained at 220°F. Injections were made every eight minutes. The limitation this imposed was recognized early on, but it was thought that the source emissions may be steady enough for accurate assessment despite the data point limitation. Average non-methane organic concentrations as determined by the instrument's integrator were reported as ppm VOC. Carbon monoxide values were also reported in ppm concentrations.

Table 3 shows the comparative results from the two methods in terms of concentration. The analyzer VOC and CO results are significantly lower than the Method 25 results in all cases.

TABLE 3 BOILER H - COMPARISON OF VOC AND CO EMISSIONS DETERMINED BY EPA METHOD 25 AND A BYRON 401S HYDROCARBON ANALYZER (BAGASSE FIRED BOILER) TEST DATE 2/4/83

	NCASI METHOD 25		CONTRACTOR (ESE) BYRON 401S ANALYZER	
TEST	CO (ppm)	VOC (ppm)	CO (ppm)	VOC (ppm)
1	1388	74	*807+	47
2	2268	137	*182+	*67+
3	1644	439	1320	99

*These averages contain offscale peak values; see text.

Three problems were encountered with the use of the hydrocarbon analyzer, which led to the low values. First, VOC and CO concentration fluctuations within the boiler were far more significant than anticipated. Since high concentration spikes were short-lived by nature, it was impossible to grab a representative sample. Second, the contractor experienced some difficulty in maintaining the sample line temperature, which contributed to VOC loss. And third, a CO_2 interference of 3.3 ppm non-methane response per percent CO_2 caused a large correction factor to be applied to the VOC data. The concentration fluctuations severely limited the effectiveness of the analyzer due to its eight minute cycle time. Unfortunately, the contractor could not run the instrument in the direct FID injection mode (sample every two minutes), since this monitoring contract required simultaneous CO sampling. (In the direct injection mode, the 401S analyzer fills Method 25A requirements.)

The low sample line temperatures probably contributed to VOC losses, but the short piece of unheated sample line inside the instrument which was only warmed to about 160°F was a limiting factor regardless of sample line temperature. The contractor made no attempt to flush any condensed organics from the sampling lines.

The CO_2 interference in the instrument's non-methane response varied with each injection, but it was not possible to measure the CO_2 concentration with each injection, since the CO_2 cycle injection occurs at the conclusion of the NM-CO-CH_4 cycle and would not represent the CO_2 level injected in that earlier cycle. Instead, the average CO_2 level, as determined by Method 25, was used to calculate the average non-methane interference for each run. This average value, on the order of 50 ppm, was then subtracted from the uncorrected non-methane values, which were on the order of 100 to 150 ppm. This technique introduced the potential for significant unquantifiable error.

The Byron 401S hydrocarbon analyzer did not yield results equivalent to Method 25 when measuring VOC and CO emissions from an industrial boiler on-site due to (a) the fluctuating nature of the source emissions and the instrument's eight minute cycle time that significantly limited its ability to average high concentration spikes; (b) a variable CO_2 interference that could only be estimated when operating the instrument on-site.

D. Infrared Spectrometer Method

A sample was drawn from the stack through a glass fiber filter, an ice bath dropout condenser, a Teflon diaphragm pump, and then pushed through an Infrared Industrial Model 711 Hydrocarbon Analyzer. The instrument was calibrated with propane and results were presented as both ppm propane and ppm methane. This method was meant to approximate Method 25B, with the exception of the ice bath condenser. It was noted that the addition of this moisture removal device would also remove some heavier organic compounds. However, this step was necessary to protect the IR from the high moisture levels of the flue gas. This moisture would otherwise condense on and damage the cooler surfaces of the inorganic salt crystal windows in the instrument.

Comparative results for the two methods are tabulated in Table 4. It is evident from these data that the methods are not equivalent. The IR results ranged from 165 to 390 ppm (as CH_4), with an average of 235 ppm, while the Method 15 values ranged from 290 to 975 ppm (as CH_4), with an average concentration of 564 ppm. The IR values ranged from 35 to 57 percent and averaged 44 percent of the Method 25 values. The moisture dropout condenser was thought to be the major source of hydrocarbon loss, but no attempt was made to analyze the condensate.

TABLE 4 BOILER J: COMPARISON OF VOC EMISSIONS DETERMINED BY EPA METHOD 25 AND METHOD 25B (INFRARED SPECTROMETER)

RUN	STEAM PRODUCTION RATE (lb/hr)	VOC RESULTS, PPM AS CH_4 NCASI-Method 25	Contractor IR
1	90,000	975	390
2	75,000	631	240
3	50,000	559	195
4	60,000	415	225
5	90,000	514	195
6	40,000	290	165
	Average	564	235

Another point of non-equivalency between the methods is inherent in the technique of measuring different organic compounds using one wavelength of infrared light. Response factors will vary among the different compounds, and no attempt was made to determine the extent of the variance in compounds likely to be present in boiler emissions. The method is intended for use on well characterized sources whose VOC emissions are primarily alkanes, alkenes, and aromatic hydrocarbons.

V SUMMARY OF VOC EMISSION FACTORS DETERMINED BY METHOD 25 FOR WOOD-RESIDUE FIRED BOILERS AND THERMOMECHANICAL PULPING OPERATIONS

A. Northwestern Wood-Residue Fired Boiler VOC Emission Study Summary

(1) Four wood-residue fired boilers operated on fuel derived from Douglas fir were sampled for VOC and carbon monoxide emissions using Method 25. Results are listed in Table 5, along with boiler sizes and capacities.

TABLE 5 NORTHWEST WOOD-RESIDUE FIRED BOILER VOC EMISSION DATA

VOC AS CH_4		CO		STACK O_2, PERCENT	STACK MOISTURE, PERCENT	AVERAGE STEAM PRODUCTION, K lb/hr
lb/10^6 Btu	ppm	lb/10^6 Btu	ppm			
Boiler A						
0.06	100	3.25	3000	7.5	-	145
0.19	190	3.03	1750	11.2	-	75
0.22	310	-	3050	10.5	-	125
0.18	190	1.20	740	11.5	-	130
0.10	140	0.64	640	7.3	12.3	135
0.14	210	0.31	260	7.8	25.3	100
0.08	100	0.38	300	8.4	17.4	100
0.05	76	2.16	2230	8.0	11.7	130
0.21	316	1.45	5610	7.0	15.3	130
0.04	53	0.42	350	9.0	16.0	140
0.06	63	0.66	410	8.6	16.3	100
0.06	75	1.50	1010	11.5	12.6	105
Boiler B						
0.03	79	0.042	48	6.0	16.6	300
0.10	180	0.091	97	6.8	15.3	350
0.09	120	0.417	641	5.4	-	475
0.08	100	0	0	9.5	20.9	350
0.07	60	0.604	273	12.5	7.0	250
0.04	30	0.539	255	11.6	10.6	250
0.04	40	0.249	156	7.8	13.9	410
0.07	80	0.110	70	7.8	12.3	420
Boiler C						
0.06	61	1.44	900	11.0	9.7	100
0.14	116	4.00	1900	12.1	15.0	80
0.08	74	2.92	1570	11.6	15.5	90
0.08	84	2.99	1460	11.3	15.9	100
0.08	77	2.71	1640	12.0	12.0	110
0.08	84	2.29	1420	11.3	16.8	100
Boiler D						
0.03	41	0.117	87	8.9	13.9	300
0.05	70	0.151	116	8.9	13.3	300
0.05	78	0.224	217	7.4	17.7	340
0.04	71	0.144	148	7.2	18.7	350
0.06	99	0.242	230	6.6	13.9	350
0.06	84	0.291	252	8.8	13.3	340
0.04	61	0.243	212	9.3	19.4	300
0.05	71	0.537	410	10.2	11.9	275

to organics stripped from the scrubber waters. (The low and high after-scrubber VOC emission rates were from two side-by-side units, Boilers C and D, respectively, that both used pre-dried fuel from a bark dryer that operated on Boiler D's exhaust. All of the bark dryer emissions exited through Boiler D's scrubber. The average VOC emission rate from these two units, 0.13 lb/10^6 Btu, is in the same range as the other boilers' after-scrubber rates.)

TABLE 6 A SUMMARY OF VOC AND CO EMISSION RATES FROM SOUTHERN WOOD RESIDUE FIRED POWER BOILERS

BOILER AND STEAM CAPACITY (K lb/hr)	AVERAGE STEAM PRODUCTION		O_2 (percent, wet basis)	CO (lb/10^6 Btu)	VOC (lb carbon 10^6 Btu)		
	Percent of Capacity	(K lb/hr)			Before Scrubber	After Scrubber	Difference
A (135)	85	115		1.82		0.075	-
	86	116		2.35	0.044	0.078	+0.034
	66	89		5.59	0.134	0.232	+0.098
Average	79	107		3.25	0.089	0.128	+0.066
B (135)	109	147		1.35		0.085	
	78	105		2.36	0.059	0.109	+0.050
	81	109		2.74	0.052	0.133	+0.081
Average	89	120		2.15	0.056	0.109	+0.066
C (200)	93	185	3.4	1.27	0.038	0.051	+0.013
	89	178	3.2	0.99		0.035	-
	88	176	3.0	1.07	0.008	0.029	+0.021
Average	90	180	3.3	1.11	0.023	0.038	+0.017
D (400)	93	372	3.4	0.42	Not Available	*0.277	
	97	388	3.3	0.43		*0.214	
	99	395	3.6	0.43		*0.139	
	96	384	4.0	0.51		*0.201	
Average	96	385	3.6	0.45		0.208	
E (360)	58	207	9.1	0.32	0.059	No Scrubber	
	71	254	5.6	1.56	0.046		
Average	64	231	7.4	0.94	0.053		
F (400)	101	†402	1.8	0.99	Not Available	†0.124	
	83	333	2.6	0.29		0.185	
	77	306	2.8	0.14		0.120	
	78	313	2.7	0.18		0.116	
	69	274	5.1	0.42		0.056	
Average	82	326	3.0	0.40		0.120	

*These values include emissions from a bark dryer. See text.
†A combination of bark and oil was fired during these tests.

(4) Average CO emission rates for Boilers A, B, C, D, E, and F, respectively, were 3.25, 2.15, 1.11, 0.45, 0.94, and 0.40 lb/10^6 Btu. This wide range of CO emission rates was also noted in the earlier NCASI study on boilers in the Northwest (0.24 to 2.63 lb/10^6 Btu; see Reference 5). Wet scrubbers had no significant effect on CO emissions.

(2) Average VOC emission rates were 0.10, 0.05, 0.07, and 0.04 lb/10^6 Btu for Boilers A through D, respectively.

(3) VOC emission rates appeared to be related to the percentage of total air used as overfire air. Larger percentages of overfire air use corresponded with lower VOC emissions.

(4) Average carbon monoxide emission rates were 0.47, 0.26, 2.63, and 0.24 lb/10^6 Btu for Boilers A through D, respectively. Carbon monoxide showed considerable variation and appeared to be linked to flue gas oxygen content when oil was burned in Boiler B, to flue gas oxygen content for Boiler C, and was completely random for Boiler A.

(5) An interference to the VOC sampling and analysis technique was investigated. This interference resulted from absorption of carbon dioxide in water condensed in the sample trap and the subsequent incorporation into the ice matrix in the cryogenic trap. This CO_2 was not removed from the trap when flushed with zero air. The resulting interference increased in variability and magnitude in proportion with CO_2 and increased moisture content of the sampled gas increased. For typical wood-residue fired boiler flue gases the interference was in the range of 15 to 30 ppm or 0.012 to 0.021 lb/10^6 Btu. A "warm purge" backflush technique was developed to minimize this interference. The minimum detectable for wood-residue fired boilers was 35 ppm with EPA Method 25 in this study.

B. Southern Wood-Residue Fired Boiler VOC Emission Study Summary

(1) Six wood-residue fired boilers operated on bark fuel derived from southern pine and mixed southern hardwoods were sampled for VOC and CO emissions using a modified version of EPA Reference Method 25 which effectively eliminated CO_2 interference. Five of the boilers were fitted with venturi-type wet scrubbers (for particulate control) that used some form of recycled mill water for makeup. Three of these units were tested before and after the scrubbers. Results are listed in Table 6.

(2) Average before-scrubber VOC emission rates for Boilers A, B, C, and E were 0.09, 0.06, 0.02, and 0.05 lb carbon/10^6 Btu, respectively. These emission rates are in the same range as rates measured on four boilers in the Northwest and reported earlier by NCASI (0.04 to 0.10 lb as methane, or 0.03 to 0.08 lb carbon/10^6 Btu; see Reference 5).

(3) Average VOC emission rates after a wet scrubber for Boilers A, B, C, D, and F were 0.13, 0.11, 0.04, 0.21, and 0.12 lb carbon/10^6 Btu, respectively. A net increase in VOC emissions was noted in all cases where before- and after-scrubber samples were taken. The average emission rate increases for Boilers A, B, and C were 0.07, 0.07, and 0.02 lb carbon/10^6 Btu, or 52, 61, and 45 percent, respectively. The increased rates were attributed

(5) There was no significant correlation between CO and VOC emission rates at the concentration levels tested, with one notable exception during an upset on Boiler A, when both compounds exhibited high emission rates. Based on these observations it did not seem practical to use CO as a surrogate for VOC during normal operation.

(6) Three additional residue fired boilers were tested individually using EPA Reference Method 25 concurrently with one of three alternate methods in an effort to identify an equivalent method. The first alternative method employed an EPA Reference Method 5 train with a flame ionization detector (FID) after the last ice bath impinger. A total organic carbon (TOC) analysis was run on the impinger water and the results were added to the dried acetone train rinse weight and the FID concentration values. The final total was within five percent of the Method 25 values, but the complexity and equipment costs of the alternate method exceeded those of Method 25. The second alternate method used a Byron 401S hydrocarbon analyzer with an in-stack filter and a heat traced sample line. Results were not comparable to Method 25 results due to (a) the fluctuating nature of the emissions and the instrument's eight minute cycle time limitation, and (b) uncertainty introduced by CO_2 interference when the instrument is operated in an on-site mode. The third alternate method used an infrared (IR) spectrometer with an in-stack filter, ice water condensate dropout bottle, and an unheated sample line. Results averaged 44 percent of Method 25 results. VOC losses were attributed to the moisture dropout bottle, which was essential to the protection of the IR sample chamber.

(7) The VOC emission factor for wood-residue fired power boilers listed in the January 1984 revision of AP-42 of 0.16 lb (as methane) or 0.12 lb as carbon/10^6 Btu fired is about twice as high as the average factor for emissions determined prior to a scrubber in this study. However, this value is similar to the average after-scrubber VOC emission rate of 0.12 lb carbon/10^6 Btu.

C. Thermomechanical Pulping VOC Emission Study Summary

(1) EPA-25, the reference method for the measurement of VOC, can be adapted to the measurement of emissions from refiner pulp processes. Due to the high moisture content of these emissions, calculations should be based on a moisture rather than dry gas emission rate. Either a large trap operated at -78°C or two standard size traps in series, the first operated at 0°C and the second at -78°C, is suggested for sample collection.

(2) VOC emissions from two TMP processes operated on western white wood species ranged from 1.02 to 2.15 lb carbon/ton of air dried pulp, with a daily average of 1.42 lb/ton. From western pine species emissions ranged from 0.83 to 3.40 lb/ton, with a daily average of 1.79 lb/ton. From southern pine species at three facilities emissions ranged from 2.15 to 7.61 lb/ton, and

had a daily average of 3.19 lb/ton at the mills employing impressafiners (screw presses that pretreat the chips by mixing them with hot water and squeezing), and 6.65 lb/ton at the mill without an impressafiner.

(3) The VOC emission rates were proportional to moisture emission rates for the three wood species sampled. The emission potential for white wood species was lowest, while that for southern pine species was highest. The use of an impressafiner to pretreat incoming chips was found to significantly decrease VOC emission potential.

(4) A short field study suggested that heat recovery systems designed primarily for steam recovery would be ineffective in the capture of volatile organic carbon. Heat recovery systems designed to condense water would be expected to capture volatile organics as a function of vapor pressure of the organic species present and operational temperature of the system.

VI LITERATURE REFERENCES

(1) Federal Register 45 (194) (October 3, 1980).

(2) "Proceedings of the 1981 NCASI West Coast Regional Meeting," Special Report 81-10, NCASI (October 1981).

(3) "A Study of Kraft Recovery Furnace Total Gaseous Non-Methane Organic Emissions," Atmospheric Quality Improvement Technical Bulletin No. 112, NCASI (February 1981).

(4) "A Study of Kraft Process Lime Kiln Total Gaseous Non-Methane Organic Emissions," Technical Bulletin No. 358, NCASI (September 1981).

(5) "A Study of Wood-Residue Fired Power Boiler Total Gaseous Non-Methane Organic Emissions in the Northwest," Atmospheric Quality Improvement Technical Bulletin No. 109, NCASI (September 1980).

(6) "Volatile Organic Carbon Emissions from Wood Residue Fired Power Boilers in the Southeast," Technical Bulletin No. 455, NCASI (April 1985).

(7) "A Study of Organic Compound Emissions from Veneer Dryers and Means for Their Control," Technical Bulletin No. 405, NCASI (August 1983).

(8) "EPA Method 25 TGNMO Emission Factors for the Thermomechanical Pulping Process," Technical Bulletin No. 410, NCASI (October 1983).

(9) "Method 25 Evaluation of Trap Recovery Unit Design," Report No. 82-SFS1-3-2, EPA Contract No. 68-02-3543, Pollution Control Science (1984).

AN OVERVIEW OF THE DEVELOPMENT OF METHODS OF CHEMOMETRICS

W. J. DUNN III
COLLEGE OF PHARMACY
UNIVERSITY OF ILLINOIS AT CHICAGO
833 S. WOOD ST.
CHICAGO, ILLINOIS 60612

Analytical chemists have developed methods of data analysis which are capable of detecting and accurately quantifying the components of environmental samples. As a result it is not unusual to observe large numbers of substances in such samples. Samples containing toxaphene, for example, may show as many as 200-300 components. The storage, display and interpretation of large numbers of such samples then becomes impossible without data analytic methods capable of dealing with multivariate data. This part of the symposium is designed to introduce various applications of multivariate methods of data analysis, so-called methods of chemometrics (1), to the analysis of chemical data.

A major objective of the application of such methods to air quality data is catagorization or classification of samples. This may be according to site of origin, chemical manufacturer, etc., the assumption being that a given residue contains information of a "fingerprint" nature which can be used in the identification of the samples. One of the first methods developed for such studies is discussed by Fisher (2) who at the time was attempting to catagorize agricultural crops according to varying climatic conditions. Fisher carried out monitoring experiments on plants as a function of rainfall, temperature, etc., and developed a method for optimization of interclass variance. His data were characterized as many samples described by a few variables.

In the early 1970's a number of attempts were made to apply Fisher's methods of discriminant analysis to chemical data. Such data were of much different structure than that of Fisher. The data were characterized as few samples described by many variables. The results of these applications were less than optimal.

This deficiency was realized by Wold (3) who developed a method of classification based on principal components modelling of multivariate data, the SIMCA method of pattern recognition (3). This method, not being sensitive to data characterized as few sample relative to the number of measured variables, is the method of choice for analysis of such data. A number of the presentations which follow are variations of this method.

There are a few short-comings of principal components modelling if information beyond classification or catagorization is desired. This is the case in which calibration and quantification of the components in a complex mixture is desired. An extension of principal components analysis, the partial least squares (PLS) method has been developed for this application. One presentation on the program will deal with this method.

With the advent of powerful microcomputers it is possible for such data analytic methods to be applied to routinely so such methods of data analysis will soon be "built" into the analytical process.

REFERENCES

1. Kowalski, B. R., Chemistry and Industry, 882-884, 1978.

2. Fisher, R. A., Statistical Methods for Research Workers, Boyd, London, 1978.

3. Wold, S., Pattern Recognition, 8, 127-139, 1976.

CLUSTER ANALYSIS APPLIED TO INDIVIDUAL ATMOSPHERIC PARTICLES.

T. W. Shattuck[1], M. S. Germani[2], P. R. Buseck.[3] 1. Colby College, Waterville, Maine 04901. 2. Walter C. McCrone Assoc., 2820 S. Michigan Ave., Chicago, Illinois 60616. 3. Chemistry and Geology Departments, Arizona State University, Tempe, Arizona 85287.

Individual aerosol particle analysis using the analytical scanning electron microscope, with its wealth of information on the size, shape, morphology and chemical composition of particles, is an excellent tool for source attribution and studies of particle dynamics (1). The elemental composition is determined using X-ray energy dispersive analysis (EDS). The recent introduction of completely automated analytical scanning electron microscopes (ASEM) extends the usefulness of this technique to survey studies involving many sampling sites and sampling periods. In survey studies individual particle analysis is particularly valuable since it provides information on the distribution and speciation of elements within the sample as well as overall elemental contributions. The vast amount of information from the ASEM presents a challenge to the analyst, since the characterization of about 1000 particles for 30 elements is necessary for each sample. The problem then is to condense the mass of information into a more concise form, without losing information on the elemental distribution between the particles.

Cluster analysis is a useful statistical tool for identifying the types of particles that occur in a sample. In cluster analysis particles are grouped into clusters of similar composition (2). Each cluster identifies a type of particle occurring in the aerosol. Every cluster is represented by a centroid, which is the average composition of all of the particles in the cluster. The number of particles assigned to each cluster may be displayed as a particle number versus particle type histogram. Particle number versus particle type histograms are an easy way to monitor changes between sampling sites and sampling periods. As such, these histograms represent a tremendous simplification and reduction in the volume of data, without excessive loss of information.

In order to verify a cluster analysis scheme, two things must be shown. 1) The range of particle types determined from a representative aerosol sample must be realistic and inclusive. Realistic clusters will give centroids that are identifiable as relatively homogeneous mineral or anthropogenic particle types. The results will be inclusive if few of the particles in a sample remain unassigned. In this study, a sample from the Phoenix aerosol will be used for this purpose. 2) The compositions of the centroids and the corresponding cluster assignments should reasonably reproduce bulk analysis results. This mass balance comparison is carried out by analyzing individual particles of a well characterized standard sample. In this study, USGS granite and basalt samples are used.

Results

Aerosol Particle Types The results of cluster analysis on a representative sample from downtown Phoenix are given in Table I. The details of the cluster analysis are given below. The major particle type was quartz, which accounted for 19% of the particles. Various alumino-silicate types were the next most abundant. However, the abundances of these particle types vary widely from site to site. Particles with unusual composition were not assigned clusters. Many particles rich in heavy metals were found in the unassigned group.

Table I. Cluster Composition for Representative Phoenix Aerosol Sample

Elemental Composition[a]	Similar Mineral[b]	% Abundance
Si K Al Fe	Orthoclase	7
Si Al K Fe	Muscovite	15
Si Al Fe Ca	Albite/Montmorillonite	14
Si Ca Fe Al	(Epidote)	6
Si Fe Al K	Biotite	4
Si	Quartz	19
Fe Si Al Mg	Ripidolite/Chlorite	2
Fe	Magnetite	7
Ca Si Fe	Pyroxene	4
Ca	Calcite	3
Ca S Si	Gypsum	1
Ca Si Fe	(Tremolite/Actinolite)	2
Ti Si	(Rutile)	2
Ti Fe Si		0.5
K Cl Si		0.5
Pb Cl Br		3
Pb Si		3
Fe Zn Si S		1
S Si Na		1
Unassigned		4

[a] Si indicates that Si may be present in the particles or may be due to a spectral artifact (carbon absorption edge).

[b] ( ) indicates only a possible mineral assignment for the cluster.

Many clusters were well resolved, however the alumino-silicate clusters in the Phoenix samples were probably mixtures of several mineral types. The minerals indicated in Table I have been identified in the Phoenix aerosol in the 5 to 50 micron diameter size range (3). They were listed not as absolute assignments but as suggestions for the most prominent mineral type in the given cluster. Obviously many of the particles were not necessarily crustal in origin. For example, there were many sources of iron and iron oxide particles other than magnetite.

Mass Balance Elemental composition and size data were collected for USGS standard samples of Granite, G-2 and Basalt, BHVL-1. The data set contained particles with sizes in the 1-10 micron range. The compositions, obtained from EDS region-of-interest integrals, were converted to relative abundances, with the sum of the concentrations equal to one. No other variable scaling was used. Seven methods were tested for choosing seedpoints, and gave comparable results. Initially, 15 seedpoints were used. The Forgey variety of K-means cluster analysis (2) was then used to define the clusters. The number of clusters to retain, of the initial 15, was determined in the following way. Cluster significance was tested using the ratio of the between clusters sum of squared distances to the within clusters sum of squared distances (4). The cluster with the most test failures was then rejected. Using the remaining centroids as seedpoints, cluster analysis was repeated. This process was continued, rejecting one cluster at a time until the number of unassigned particles began to increase and the number of significant clusters began to decrease. Pairs of isolated but overlapping clusters were joined and clusters with few members were deleted to complete the centroid set.

A few representative particles from each cluster were chosen and reanalyzed, using a full ZAF correction scheme. These compositions, the cluster assignments and the size of each particle were used to calculate the overall composition of the sample. Each particle was assumed to be a sphere for volume calculations, and the density of the particles in each cluster was approximated by that of a similar mineral.

There were eight clusters found for the granite sample: quartz, two plagioclase, orthoclase, biotite, muscovite, chlorite and apatite. In addition several metal sulfide clusters where found, but they were deleted from the centroid set because of low abundance. For the basalt sample, seven clusters resulted: quartz, plagioclase, two calcium pyroxenes, two titanium pyroxenes and a glass phase containing large amounts of potassium and a wide mixture of other elements. The mass balance results are given in Table II.

Table II. Mass Balance Comparisons for Granite G-2 and Basalt BHVL-1. Weight fraction normalized to Si.

Granite	Na	Mg	Al	Si	Fe	K	Ca
Particle EDS	.042	.015	.234	1.0	.029	.076	.029
Accepted	.059	.011	.222	1.0	.035	.064	.028
% Error	-29	36	5		-17	19	4
Basalt							
Particle EDS	.044	.125	.283	1.0	.160	.003	.220
Accepted	.044	.143	.276	1.0	.220	.011	.228
% Error		-13	3		-27	-73	-4

The agreement between the particle and accepted results was quite good considering the level of approximations involved, except for Fe and K. In the basalt, potassium occurs predominantly in a glassy phase. When crushed this glassy phase produces very small particles which fall below the cut-off limit used in the data acquisition step. Therefore, it is not surprising that potassium is under-represented in the mass balance results. The most important mineral phase for iron is biotite mica. These particles were usually flat plates. Particles of this type will show the biggest errors when using standard ZAF correction algorithms.

Summary

The particles in the Phoenix aerosol fell into relatively homogeneous composition ranges which could be identified using cluster analysis. The resulting clusters gave a satisfactory range of particle types with only 4% of the particles left unassigned. Mass balance comparisons using the same methods on standard samples showed sufficient agreement between the individual particle results and bulk analyses.

The usefulness of these results for a long term sampling study was tested in the following way. Using the clusters found, nearest neighbor discriminant analysis was used to characterize samples from the Phoenix aerosol, taken over a two week period. The resulting particle number versus particle type histograms were used in factor analysis and showed strong correlation with upper level wind directions.

The implications of the success of cluster analysis for aerosol particles is twofold. First, the analyst need not know or specify in advance the kinds of particles that are expected in a given area. The structure in aerosol particulate data is sufficient to identify the underlying particle types. Secondly, the large volume of data available is easily condensed into a more compact form while retaining all of the advantages of individual particle analysis.

Acknowledgments

Financial support for this work was provided by grants ATM-8022849 and ATM-8404022 from the Atmospheric Chemistry Division of the National Science Foundation.

Literature Cited

1. Post, J. T.; Buseck, P. R. Environ. Sci. Technol., 1984, 18, 35-42.
2. Massart, D. L.; Kaufman, L. "The Interpretation of Analytical Chemical Data by the Use of Cluster Analysis"; Wiley: New York, 1983; p. 107.
3. Pewe, T. L.; Pewe, E. A.; Pewe, R. H.; Journaux, A.; Slatt, R. M. Spec. Pap.--Geol. Soc. Am. 1981, No. 186.
4. Hartigan, J. A. "Clustering Algorithms"; Wiley: New York, 1975, p. 97.

ABSTRACT

EVALUATION OF EMISSION DATA FROM HAZARDOUS WASTE INCINERATION TESTS USING PATTERN RECOGNITION TECHNIQUES

By

Karin M. Bauer and Dennis D. Wallace
Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

To be presented at the Fifth Annual Symposium on Recent Advances
in the Measurements of Air Pollutants,
Raleigh, North Carolina, May 1985

At each of eight incinerator facilities a series of test runs were conducted to examine particulate and HCl emission rates from the incinerators and to characterize the performance of these incinerators with respect to destruction and removal efficiency (DRE) for principal organic hazardous constituents (POHCs).

One of the chief concerns was to characterize the incinerator inputs and outputs of POHCs. Samples of waste feeds, control system makeup waters (as appropriate), stack gases, and control system effluents were collected during each run. Auxiliary fuels and incinerator ash were also sampled for selected runs. Samples were evaluated for concentrations of Appendix VIII organic constituents using gas chromatography/mass spectrometry (GC/MS). In addition, waste samples were analyzed for moisture, ash and chloride content, viscosity, and heating value. Stack gas samples were analyzed to determine particulate and HCl concentrations and concentrations of O_2, CO, and CO_2. Total hydrocarbons (THC) in the stack gas were continuously monitored. Incinerator operating characteristics such as combustion temperature, residence time, total heat input rate, and control device parameters were also monitored during each test.

One focus of the study was to analyze and quantify the impact on DREs of the parameters listed above. The analyses examined relationships between DREs and these various parameters and/or identified patterns among the observations within the two subsets of the data base: those observations for which DRE was above 99.99%, and those for which DRE was below 99.99%. Given the large amount of data, pattern recognition techniques were the most logical choice for reducing the dimensionality of the data for simpler representation and interpretation and to identify those important variables that determine experimental behavior.

Correlation, factor, principal components, discriminant, and cluster analyses were the main techniques used in the study. Engineering knowledge of the incineration process was used to define several sets of variables on which the principal component analyses were conducted. Typically, these analyses considered sets of process and waste feed parameters, continuously monitored stack gas parameters (e.g., O_2, CO, CO_2, THC), stack gas concentration of POHCs and DREs. Through the multiple analyses we examined the impact of the removal of variables such as input and/or output waste concentrations or DRE on the resulting principal components, the amount of variance different parameters explained, and within each component, the change in hierarchy and relative importance of the individual variables. Discriminant analysis was also used in order to find a linear combination of significant parameters that would best discriminate between those observations that achieved 99.99% DRE and those that failed. Cluster analysis was performed on the compounds to determine whether certain compounds or groups of compounds tend to cluster in terms of their presence and total concentration in the stack gas.

The SIMCA-3B Pattern Recognition software package for microcomputers, as well as the SAS and BMDP statistical software packages, were extensively used in the analyses and evaluation of the data. The results of the different techniques will be presented, compared, and interpreted.

DISTRIBUTED CHEMICAL ALARM SYSTEMS FOR PLANT SECURITY BASED ON ION MOBILITY SPECTROMETRY (IMS)

Joseph E. Roehl
ALLIED Bendix Aerospace
Bendix Environmental Systems Division
1400 Taylor Avenue, P.O. Box 9840
Baltimore, Maryland 21284-9840

Abstract

This paper describes work being performed at ALLIED Bendix Environmental Systems Division (ESD) to develop a chemical alarm network based on small ion mobility spectrometers, which may be distributed inside a facility or on its perimeter. Ion mobility spectrometers require a fair degree of signal processing and the processing burden must be divided up between local processors, which are attached directly to the ion mobility cells and a central microprocessor which executes an alarm algorithm, displays alarm messages, and interfaces to other computers or display systems if desired. The paper discusses ion mobility spectrometry (IMS), chemicals which (IMS) may be used to detect, the specifications for the alarm network, and the alarm algorithm in general.

INTRODUCTION

The detection of potentially hazardous chemical leaks or spills is a difficult problem especially when the material is highly toxic and small concentrations must be detected. ALLIED Bendix Environmental Systems Division (ESD) has developed an alarm technology based on ion mobility spectrometry (IMS), which is sensitive to many hazardous chemical compounds at the parts per billion (PPB) level and is suitable for monitoring applications. Figure 1 is a list of the chemical vapors which may be detected by IMS. In a typical scenario alarm units would be placed indoors and out-of-doors around processing plants, tank farms, valves, loading and unloading facilities, and the perimeter of a plant site. The alarm units would contain a sensor and a microprocessor which communicates with plant operators through a central alarm console. Very low concentration vapors released from leaks or spills would be sensed by the alarm units and plant operators would be alerted.

An alarm system used in this type of application should have the following characteristics:

- Specificity - The alarm system should only alarm to target chemicals. It will be used in a dirty industrial environment and should reject other chemical compounds.
- Sensitivity - The alarm should be sensitive to target chemicals at well below their hazardous levels.
- Logistics - The alarm should be easy to test, reliable, low power, and required a minimum of maintenance.
- Cost - The alarm should be inexpensive so that many alarm stations can be installed around a site.

An IMS system is extremely attractive for this type of application because it has the following attributes:

- High sensitivity
- No wet chemicals
- Minimal maintenance
- Low power
- Operates over a wide environmental range.

Competitive techniques rely on wet chemical systems which require frequent maintenance, relatively large gas chromatographs, or more complex technologies.

There are two potential disadvantages to IMS:

1. The device utilizes a radioactive source (Ni^{63}-Beta emitter) which requires a license and some special handling, and
2. The IMS instrument is not as selective as other chemical instruments and requires additional signal processing of the sensor output to determine if a target chemical is present.

The former problem is easily overcome and the latter problem has been overcome in the ESD design through the development of sophisticated signal processing techniques. Prototype IMS alarm systems have been constructed and tested at ESD with very favorable results. They are stand-alone systems however and must be reconfigured into sensor systems for application to a fixed facility.

THE ION MOBILITY SPECTROMETER

The heart of the alarm system described here is an ion mobility spectrometer (IMS). Ion mobility spectrometers in various forms have been around for many years. Figure 2 is a pictorial diagram of a Bendix ESD design. The cell is made up of two contiguous cylinderical sections - the reaction tube and the drift tube separated by a shutter grid. Both tubes are made up of conducting rings, separated by insulators, which are biased using external resistors to provide a uniform potential gradient through both cylinders. When gas molecules enter the reaction tube they are ionized by the Ni^{63} radioactive source. Either positive or negative ions are attracted down the reaction tube toward the drift tube depending on the direction of the electric field vector. Electric field vector direction may be changed by reversing the polarity across the resistor network. A shutter grid is placed between the reaction tube and the drift tube which functions like a camera shutter allowing ions to pass through it into the drift tube when open and annihilating ions when closed. The grid is made up of parallel wires which may be electrically shorted together at a potential equal to the magnitude of the field at the appropriate point in the coaxial electric field. This allows most ions to pass. Normally the grid is biased to create a field perpendicular to the field through the cylinders thus annihilating the ions. Ions that pass through the grid are detected at the end of the drift tube when they impact on a plate mounted in a Faraday cage. The Faraday cage surrounding the plate is necessary to reduce currents induced in the plate circuit by stray charge and the ions moving down the tube. An electrometer amplifier mounted on the back of the cell amplifies the minute current (10^{-12}A) at the plate and converts it to a voltage signal.

Figure 3 is a typical IMS positive mode signature with the trigger pulse superimposed on it. An IMS signature is a plot of ion current versus time. When the trigger pulse momentarily (10 microseconds) opens the shutter grid a cloud of ions is allowed to pass into the drift tube. The ions in the cloud under go collisions and separate themselves out by molecular weight and collision cross section. The result is that the cloud of ions entering the drift tube separates into a number of clouds each with a Gaussian profile. When successive clouds impact on the plate they produce Gaussian shaped current peaks in the plate circuit. A Gaussian peak can be completely described by the three parameters - time of peak maximum, full width half maximum (FWHM) of the peak, and height of the maximum. In an IMS all peaks tend to have the same FWHM, the height of a peak is related to the concentration of an ionic species, and time of the peak maximum relative to the center of the trigger pulse is dependent on the particular ionic species and is called the drift time. Drift time for a given ionic species is dependent on a number of parameters such as length of the drift tube, atmospheric pressure, and temperature but may be normalized to yield reduced mobility μ_0. Reduced mobility is dependent only on the particular ionic species. Unfortunately, different ionic species can have similar reduced mobilities and IMS is a low resolution technique.

In order to use an IMS as the sensor in a chemical alarm system which will only alarm to certain chemical compounds, additional specificity must be built into the system. In laboratory applications IMS is used in a controlled environment with nitrogen as a carrier gas. Sample is introduced into the gas stream for analysis. In an alarm application, however, a sampling system "snifs" ambient air which may contain a number of substances which produce IMS peaks. In order to make IMS practical for an alarm application additional chemical, electronic and software filtering must be provided in the system. It is also very desirable in an alarm system to eliminate the requirement for special carrier gas. In the ALLIED Bendix ESD design nitrogen is replaced by clean air circulating behind a permeable membrane. In addition, the IMS signal is analyzed with a microprocessor. Again, refer to Figure 3. It is representative of an IMS signature from an IMS cell embedded in the ESD alarm system. Note that there are four peaks illustrated in the figure. The first two peaks are usually present in IMS signatures. They are formed from the ionization of ammonia and water present in the air. In clean air only the NH and H+ peaks would appear. When a chemical compound with a higher proton affinity permeates into the system, charge is transferred from the H+ ions to form ions of the new material called product ions. The total charge in the ion cloud and thus the total area under the IMS signature is theoretically equal to a constant. As material enters the IMS cell it starts at a low concentration producing a monomer peak which is a combination of the new product ion and water. As the concentration of the material in the system rises the monomer peak grows at the expense of the reactant ion peak. Eventually a dimer peak appears and grows at the expense of the reactant ion and monomer until at very high concentration only the dimer appears. If the material is now stopped from entering the system, the corcentration diminishes and the process is reversed.

Figure 4 is a pictorial diagram of a Bendix ESD-designed IMS cell which contains the membrane holder, ionization source, reaction tube, and drift tube. Sample gas flows into the cell, washes the membrane, and exhausts from the cell. Clean dry air is pumped over the back of the membrane and into the IMS reaction tube. This flow of air is called the carrier flow.

A counter flow of air passes over the inside wall of the cylinderical drift tube called the drift airflow. This airflow keeps the walls of the drift tube clean.

ALARM ALGORITHM

A major problem in using IMS for alarm applications is the specificity required for a practical alarm system. Plant operators will tend to disregard any alarm system with even a low false alarm rate. Two features in the Bendix design provide the required alarm specificity: the membrane and the alarm algorithm implemented in microprocessor software. Figure 5 is a block diagram of the alarm algorithm. Analog data from the cell is digitized and analyzed by the microprocessor using the alarm algorithm which consists of a feature extractor and a pattern classifier. The feature extractor filters out high frequency noise, deconvolves partially overlapped peaks, measures the position and height of the deconvolved peaks, and normalizes the peak position relative to a reference peak to eliminate temperature and atmospheric pressure effects on the measurement. The normalized peak position is related to the reduced mobility by a constant. A table of normalized peak positions and peak amplitudes is passed to the pattern classifier portion of the algorithm. The pattern classifier portion of the algorithm is a two-step process. In the first step normalized peak positions are checked against tolerances around the expected reduced mobilities of the target chemicals. In the second step the set of peak positions and amplitudes constituting the sample measurement is treated as a vector. The dot product between the sample vector and a set of linear discriminant functions is calculated. The set of linear discriminant functions is predetermined by collecting data on the target chemicals and interferents and calculating a linear discriminant function which separates them.

STAND-ALONE ALARM SYSTEMS DEVELOPED AT ESD

Figure 6 is a block diagram of a prototype stand-alone alarm system developed at Bendix Environmental Systems Division (ESD). The system is made up of five basic blocks:

1. Sampling System - Draws ambient air into the system, provides chemical filtering by use of a membrane, and interfaces with internal air system.

2. IMS Cell - Transduces the chemical signal into an electrical signal. The output signal is ion current versus time.

3. Microcomputer - Digitizes and analyzes IMS cell signal. Implements an alarm algorithm based on pattern recognition and interfaces with the operator.

4. Pneumatic System - Contains a dual diaphragm pump which moves air through the system and a scrubber which scrubs the recirculating air passing from the sampling system to the IMS cell. An important advantage of the IMS instrument over other instruments is that it requires no external gas supply or vacuum system.

5. Operator Interface - The operator interface includes a display to alert the operator of alarms and the instrument's status, and a three-position toggle switch for the operator to select instrument mode.

DISTRIBUTED ALARM SYSTEMS UNDER DEVELOPMENT AT ESD

Figure 7 is an illustration of the distributed IMS system under development at ALLIED Bendix ESD. This system is made up of remote stations containing a sampling system, IMS cell, pneumatic system, and one chip microprocessor, and a central computer which acts as an operator interface. The local microprocessor control the IMS cells, format data, and exercise built-in-test functions. A number of local units can be tied to a single central annunciator. The central portion of the chemical detection and alarm algorithm. Target chemical substances can easily be added or deleted from the alarm list in the annunciator.

CONCLUSIONS

Chemical alarm systems based on IMS appear to be feasible and cost effective. ALLIED Bendix ESD is actively pursuing an in-house development program to demonstrate a distributed alarm system.

REFERENCES

[1] Roehl, Joseph E., "A Microprocessor-Controlled Chemical Detection and Alarm System Based on Ion Mobility Spectrometry", IEEE Transactions on Industrial Electronics, Vol. 32, No. 2, May 1985.

[2] Campbell, D.N., Carrico, J. P., and Spangler, G.E., "A Compact Ion Mobility Spectrometer System", Paper 91, Pittsburg Conference on Analytical Chemistry and Applied Spectroscopy (Atlantic City, N.J. 1983.

- Alkanes
    - Normal
    - Halogenated
- Aromatics
    - Aliphatic
    - Halogenated
    - Nitrated
- Alcohols
- Ethers
    - Normal
    - Thioethers
    - Mercaptans
- Carboxylic Acids and Esters
- Ketones

- Carbonyls
- Amines/Pyridines
- Nitrosamines
- Phenols
- Biphenyls (Halogenated)
- Phthalic Acids
- Organophosphorous Compounds
- Freon
- Herbicides
- Pesticides
- Illicit Drugs
- Explosives
- Petroleum Products
- Musk Ambrette

Figure 1. Vapors Analyzed by IMS

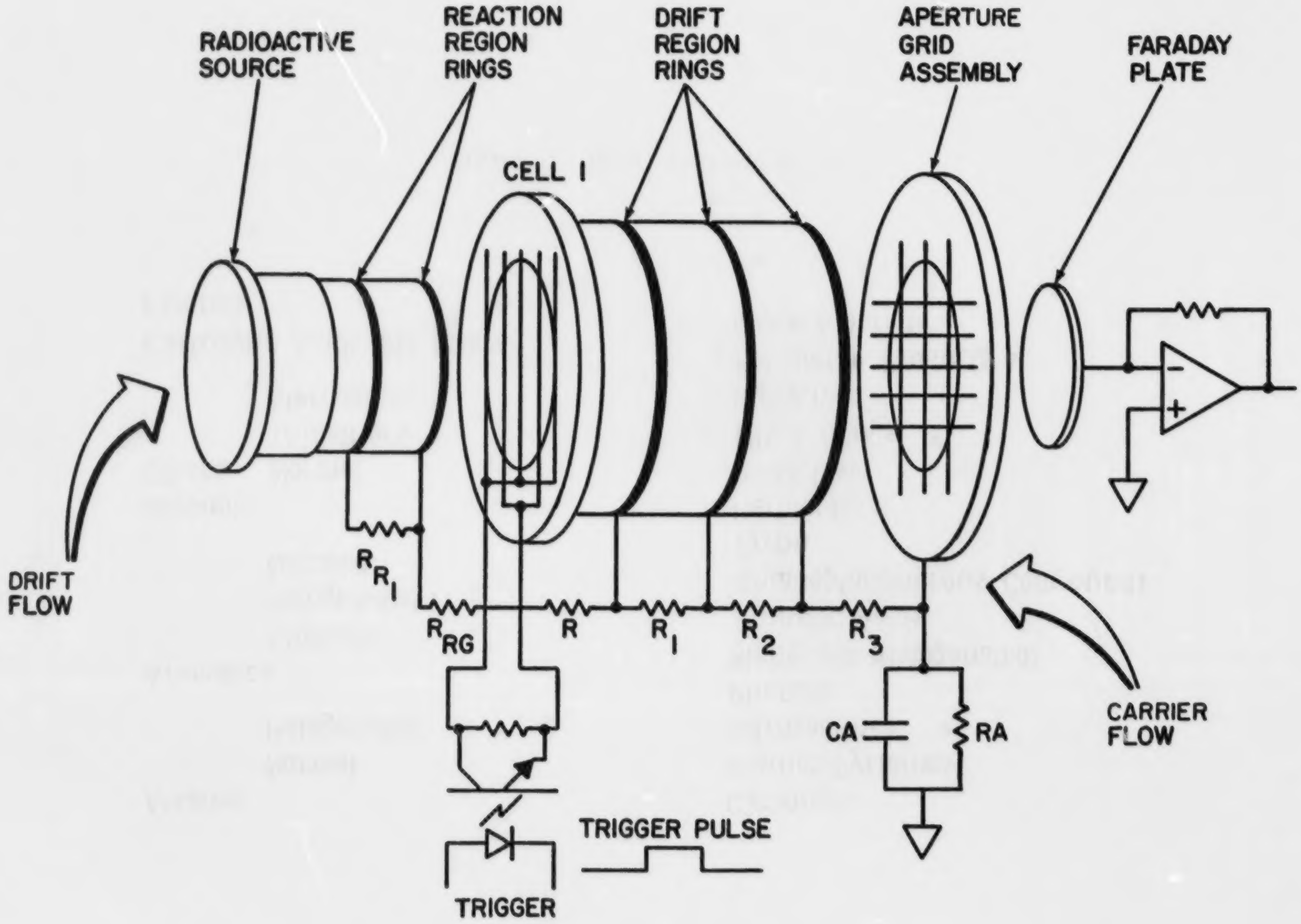

RADIOACTIVE SOURCE
REACTION REGION RINGS
DRIFT REGION RINGS
APERTURE GRID ASSEMBLY
FARADAY PLATE
CELL I
DRIFT FLOW
CARRIER FLOW
R_{R_1}
R_{RG}
R
R_1
R_2
R_3
CA
RA
-
+
TRIGGER PULSE
TRIGGER

Figure 2. IMS Cell

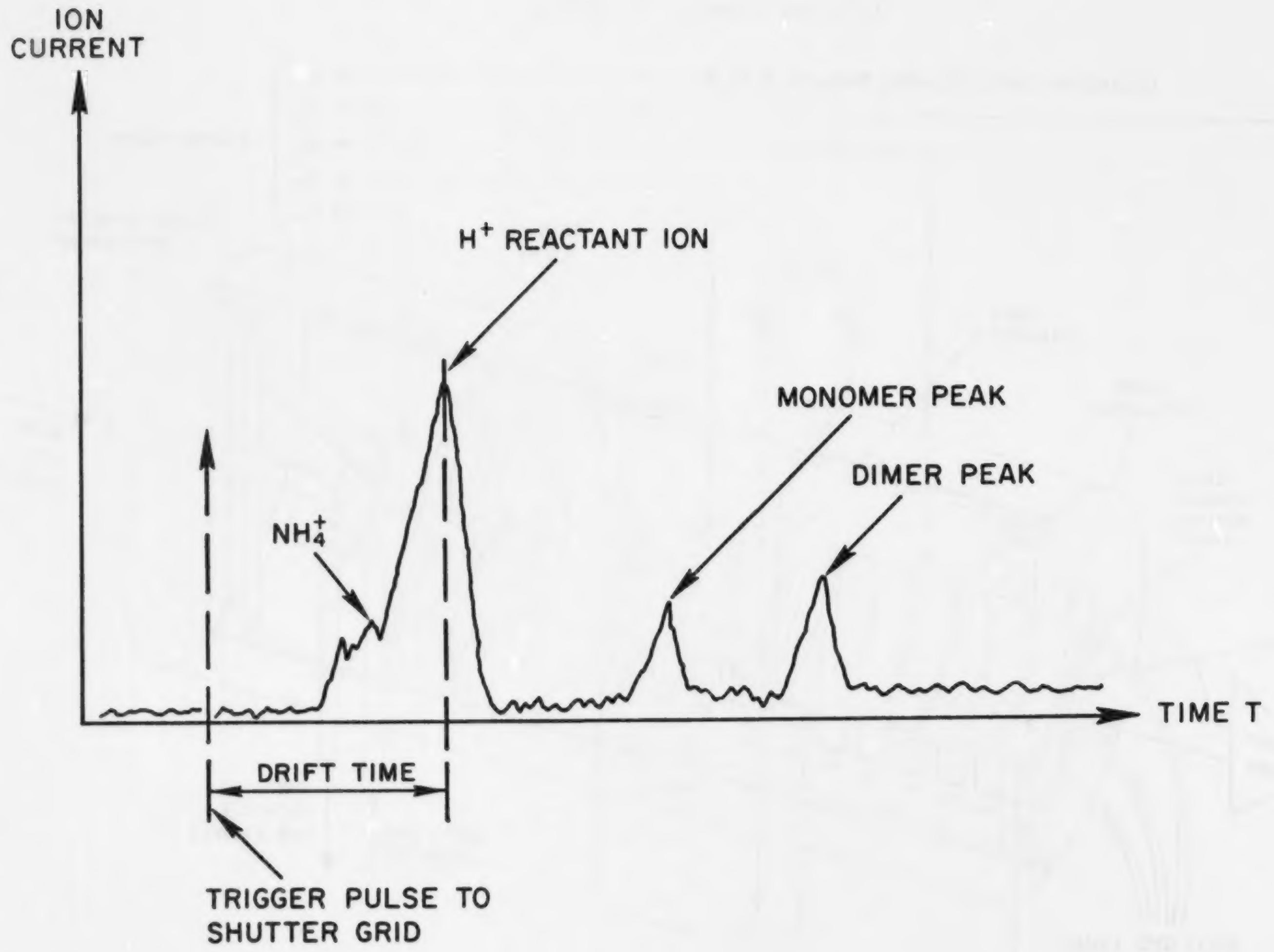


Figure 3. Typical Positive Mode IMS Signature from IMS Cell Embedded in ESD Alarm System

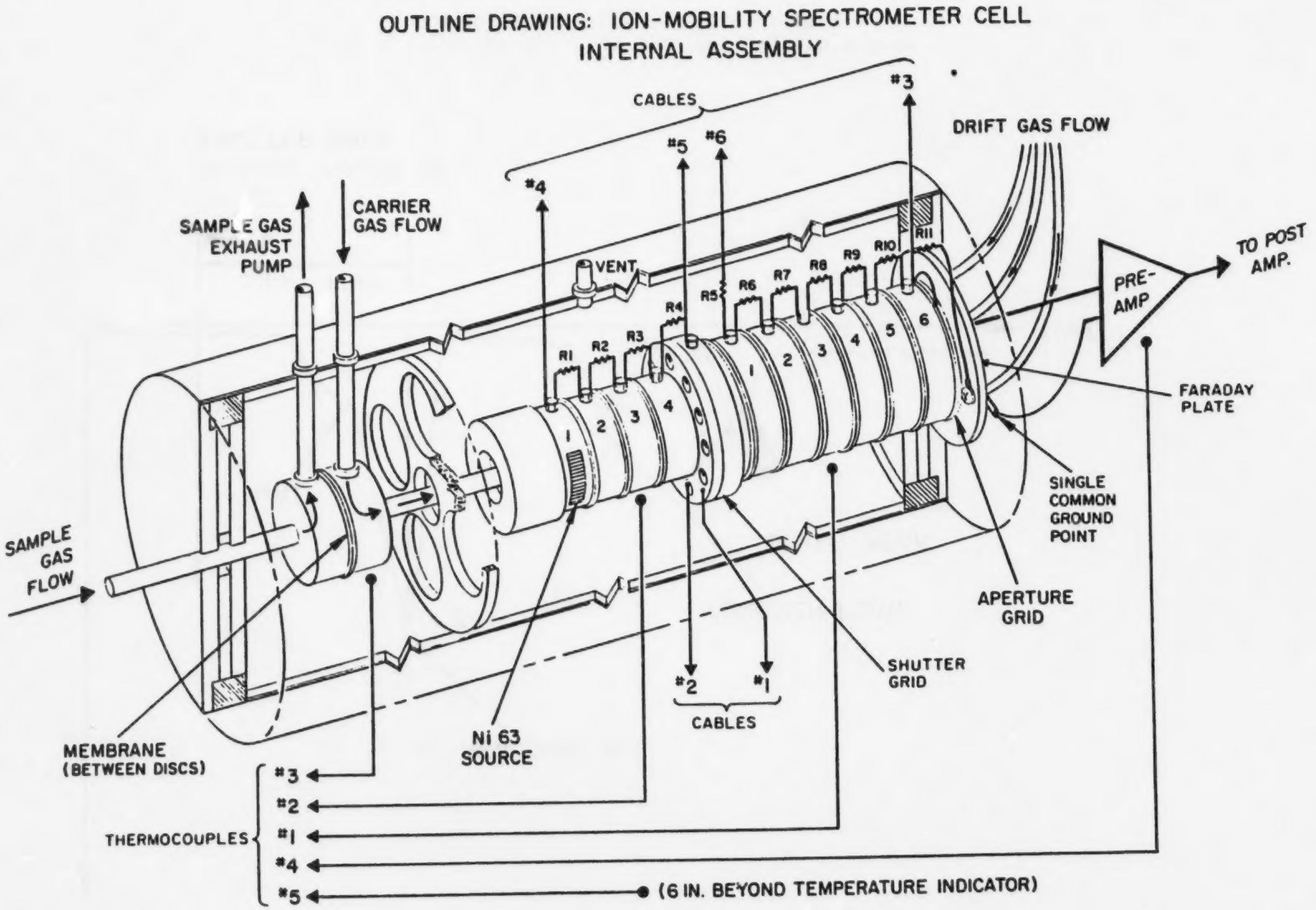

OUTLINE DRAWING: ION-MOBILITY SPECTROMETER CELL
INTERNAL ASSEMBLY
CABLES
#4
#5
#6
#3
DRIFT GAS FLOW
SAMPLE GAS EXHAUST PUMP
CARRIER GAS FLOW
VENT
R1
R2
R3
R4
R5
R6
R7
R8
R9
R10
R11
1
2
3
4
1
2
3
4
5
6
PRE-AMP
TO POST AMP.
FARADAY PLATE
SINGLE COMMON GROUND POINT
APERTURE GRID
SHUTTER GRID
SAMPLE GAS FLOW
#2
#1
CABLES
MEMBRANE (BETWEEN DISCS)
Ni 63 SOURCE
THERMOCOUPLES
#3
#2
#1
#4
#5
(6 IN. BEYOND TEMPERATURE INDICATOR)

Figure 4. Bendix IMS Cell

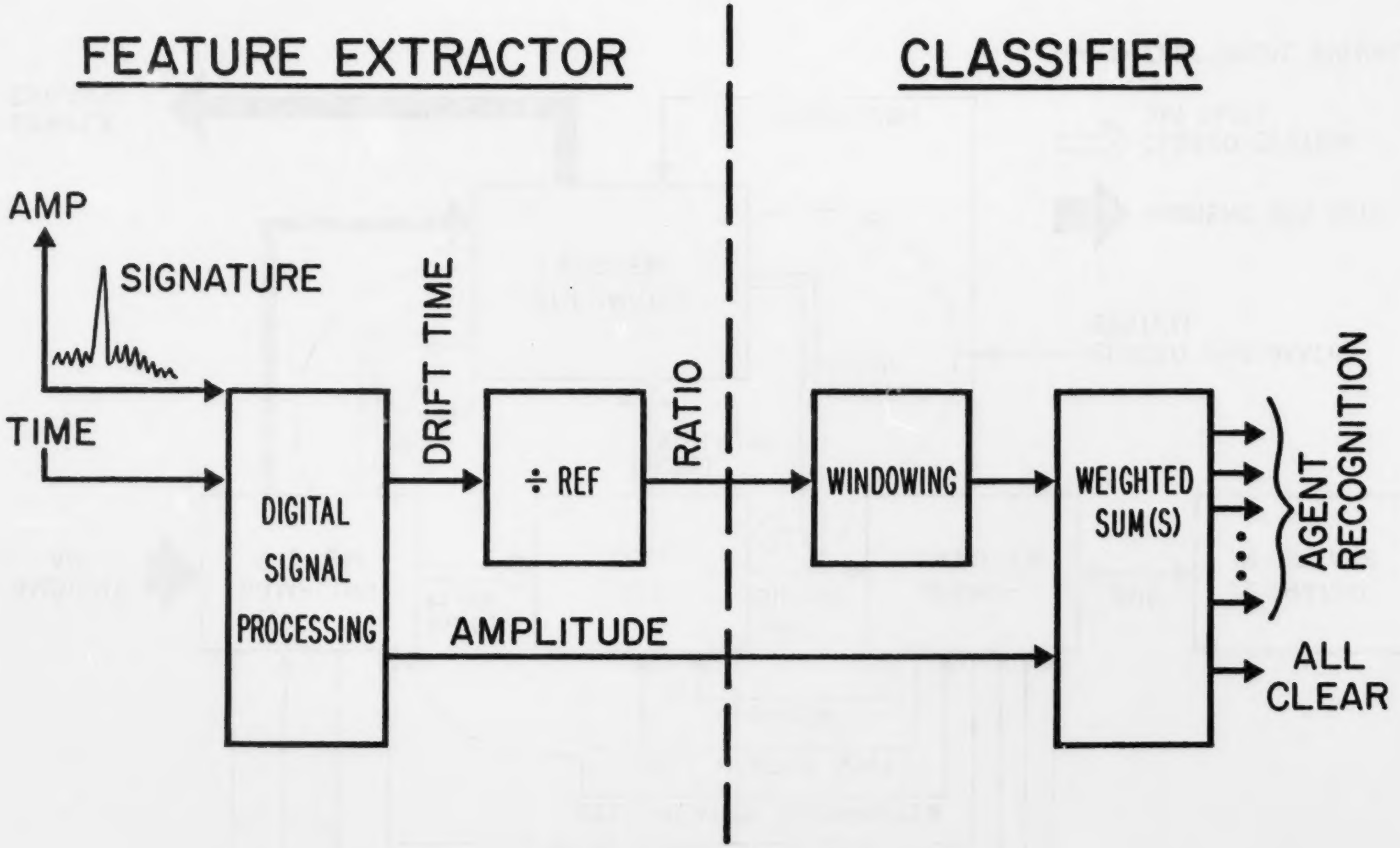
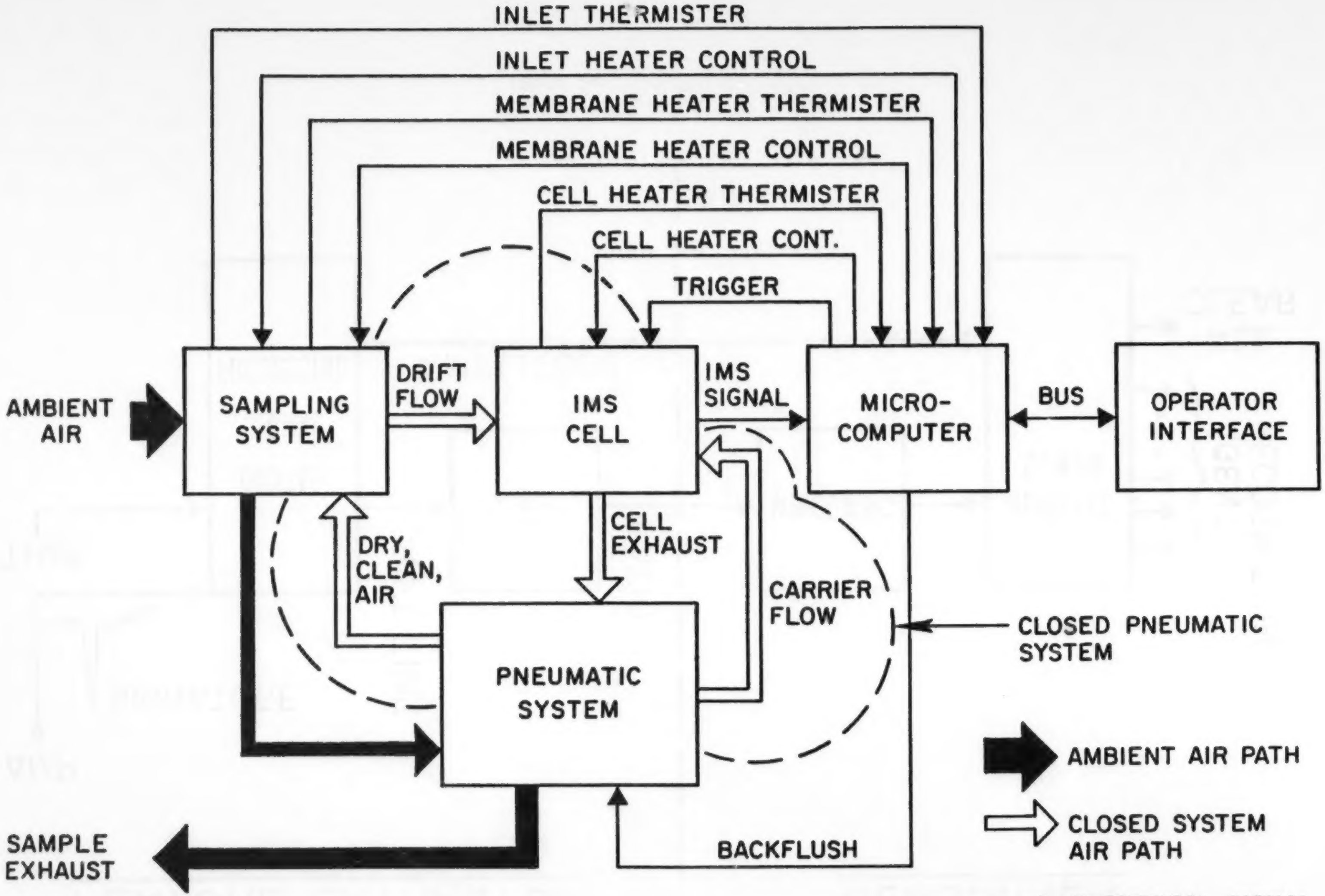

FEATURE EXTRACTOR
CLASSIFIER
AMP
SIGNATURE
TIME
DIGITAL SIGNAL PROCESSING
DRIFT TIME
÷ REF
RATIO
WINDOWING
AMPLITUDE
WEIGHTED SUM(S)
AGENT RECOGNITION
ALL CLEAR

Figure 5. Alarm Algorithm



INLET THERMISTER
INLET HEATER CONTROL
MEMBRANE HEATER THERMISTER
MEMBRANE HEATER CONTROL
CELL HEATER THERMISTER
CELL HEATER CONT.
TRIGGER
AMBIENT AIR
SAMPLING SYSTEM
DRIFT FLOW
IMS CELL
IMS SIGNAL
MICRO-COMPUTER
BUS
OPERATOR INTERFACE
DRY, CLEAN, AIR
CELL EXHAUST
CARRIER FLOW
CLOSED PNEUMATIC SYSTEM
PNEUMATIC SYSTEM
SAMPLE EXHAUST
BACKFLUSH
AMBIENT AIR PATH
CLOSED SYSTEM AIR PATH
ELECTRICAL SIGNAL

Figure 6. Alarm System Based on IMS

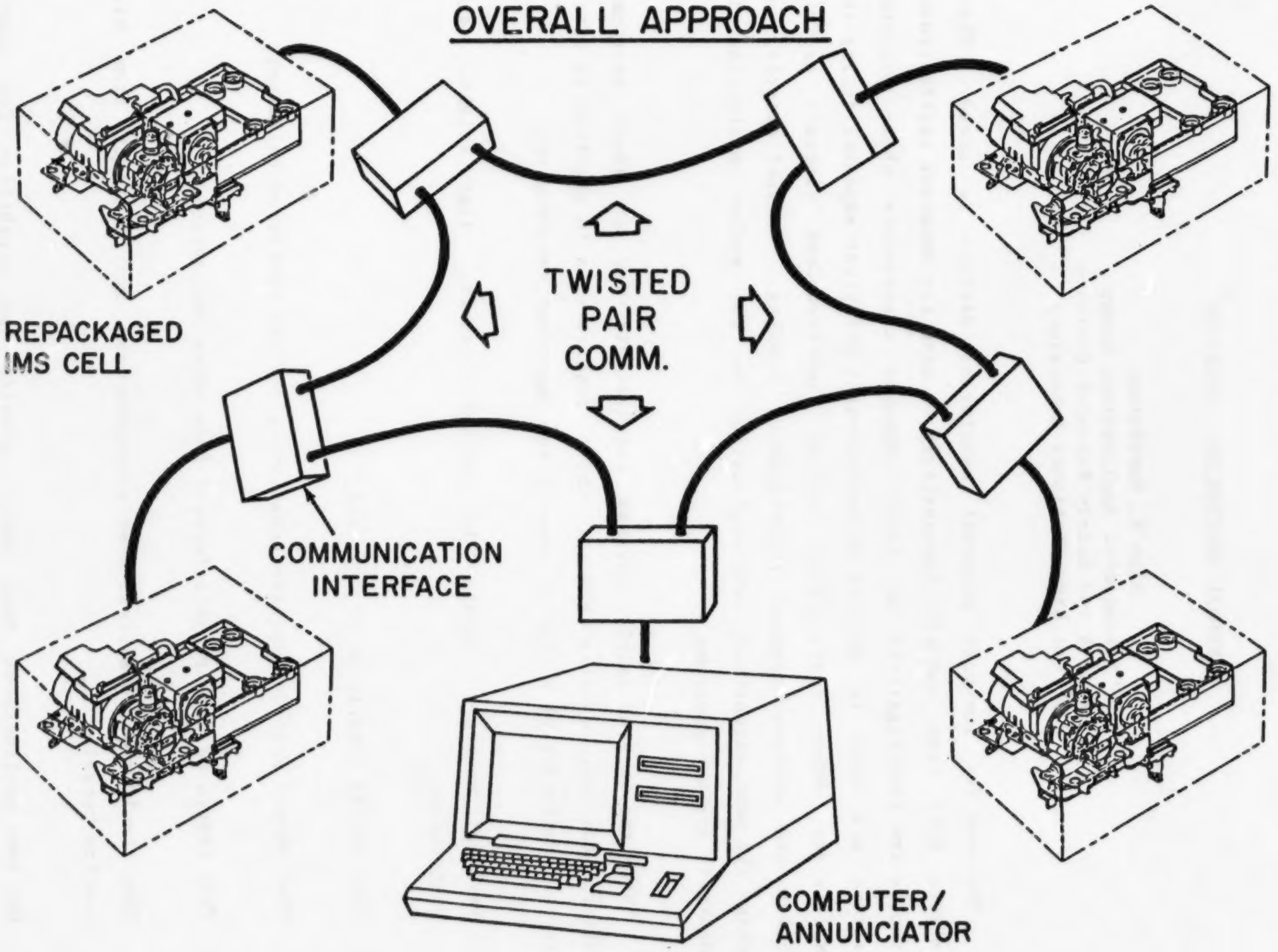

OVERALL APPROACH
REPACKAGED IMS CELL
TWISTED PAIR COMM.
COMMUNICATION INTERFACE
COMPUTER/ ANNUNCIATOR

Figure 7, Distributed IMS System

PERSONAL MONITORING: OVERVIEW*

Alan R. Hawthorne
Measurement Applications Group
Health and Safety Research Division
Oak Ridge National Laboratory

The need for low-cost personal monitoring devices is great. These monitors have been and will increasingly be used for numerous applications. Examples are investigations of total exposure assessments where personal monitors are used to measure an individual's pollutant exposure during the complete day. Other applications include time-dependent exposure profile studies and microenviromment apportionment studies. A final example, and perhaps the most extensively used application, is for worker monitoring in industrial hygiene programs.

There are several fairly obvious requirements for an ideal personal monitor; however, meeting all of these requirements in practice is often elusive. Following is a list of some of the important requirements.

1. Personal monitors should be portable--small, light weight, and unobtrusive.

2. They should ideally be of low cost.

3. They should provide adequate sensitivity for the monitored pollutant.

4. They should be free of interference from other pollutants.

5. They should require minimal user attention and not distract from his routine behavior.

6. For some applications, they should provide the capability for time-dependent exposure profiles.

---

* Research sponsored by the U.S. Department of Energy, under contract DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.

By acceptance of this article, the publisher or recipient acknowled the U.S. Government's right to retain a nonexclusive, royalty-fre license in and to any copyright covering the article.

These requirements are often hard to meet for many pollutants of interest and trade-offs must be made the various requirements. Some of the requirements are similar to those of fixed-station and portable monitors while others are substantially different.

Personal monitors can be classified into general categories based on their operation and the type of information provided. One classification distinguishes whether the monitor is an active device using a pump and requiring a power source or a passive device sampling by diffusion or permeation and requiring no power. The advantages of a passive device are obvious, and such a device is often the preferred monitor provided that important factors such as sensitivity, accuracy, and time resolution are adequately addressed. Depending on the particular application, monitors capable of providing integrated or time-dependent exposures may be preferentially desired. A second useful classification is whether the personal monitor provides time-dependent (in some cases real-time) information, or whether the result is an integrated or time-weighted average response. Most often these statements lead most readers to infer 3 passive monitors that yield time-dependent data.

There are several pollutants for which commercial or developmental passive monitors exist. Examples include formaldehyde, nitrogen dioxide, sulfur dioxide, radon, and volatile organic compounds. Passive monitors are most often of the integrating type and frequently require subsequent laboratory analysis to provide the exposure estimate.

To advance the performance of passive devices as personal monitors, there are several areas that need attention. Perhaps the greatest need is to extend the number of pollutants for which passive monitors are available. Improved sensitivity is often a limiting factor in the acceptability of passive devices and deserves continuing attention to improve performance. Another important factor that would enhance the acceptability of passive monitors is a better assessment of factors that affect precision and performance. Intercomparisons of monitor performance under field conditions would help address this issue.

Integrating samplers based on pumping air through collection devices constitute another large class of personal monitors. A wide variety of collection devices are used, including sorbent traps (for collecting volatile organic compounds), filter media (for collecting particulate matter), and impingers (usually used only as a last resort).

Items that would advance the performance of pumped collection systems include improved pump performance, improved sorbents, and better analytical techniques. Smaller, quieter, higher flow rate pumps (available at low cost) with extended battery life would address many of the problems encountered in this type of personal monitoring. A better selection of sorbents that have high sorption efficiency and yet can be quantitatively desorbed would be desirable. Finally, improvements in performance of the analytical process would result in less material being needed from samplers, thus lessening the requirements of the monitoring device.

Direct-reading personal monitors have both advantages and disadvantages to offer the user. Among the advantages are the ability to provide real-time exposure profiles and to monitor peak levels. The immediate response capability of this type of monitor may be critical in some applications, and in others the ability to avoid frequently long delays associated with laboratory analysis is certainly desirable. Frequent disadvantages of real-time personal monitors are relatively high cost, size and weight greater than for passive monitors, and limited availability for many pollutants.

Needed advances for direct-reading personal monitors include reduction in cost, increased miniaturization resulting in reduced size and weight, and development of a wider selection of microsensors. Perhaps the most challenging and difficult aspect will be development of low-cost, yet sensitive microsensors compatible with today's microelectronics. There have been dramatic advancements in the supporting microelectronics required for direct-reading personal monitors and portable data loggers. Dramatic cost reduction, increased capacity and capability, and decreased power requirements have been achieved for microprocessors and solid-state memory. Important advances have also been made in analog-to-digital and digital-to-analog converters as well.

I believe that we will see personal monitors play an increasing role in characterizing exposure levels in ambient, indoor, and occupational environments. The need clearly exists for such capability, and continuing advancements in various technologies will help provide desirable personal monitors to meet these needs.

The next several papers will provide examples of some of the recent advances in various personal monitors. They include papers on pumped sampling methods, passive devices, and direct-reading monitors.

INDOOR AEROSOL IMPACTOR

William Turner and John Spengler
Department of Environmental Science & Physiology
Harvard School of Public Health
Boston, MA

Virgil Marple
University of Minnesota
Minneapolis, MN

INTRODUCTION

An aerosol impactor and constant flow pumping system designed for indoor sampling has been developed as part of the ongoing Harvard Air Pollution Epidemiologic Study. This impactor is designed to sample at a flow rate of 4 lpm. A double impactor was used to increase efficiency of particle separation. Two units have been designed to provide a sharp 50 percent cutoff at 2.5 um and 10.0 um. Testing has also been conducted to determine the effect of flow rate on the size cut characteristics. The system has been designed to provide uniform deposition on 37 mm Teflon filters mounted on 2" x 2" plastic holders. The collected material is particularly suitable for automated analysis using XRF and other techniques.

This device was deployed in conjunction with a constant flow sampler in 300 homes during the winter of 1984-85 in Watertown, MA and will be used to make measurements in 2000 homes in the next four years. The design criteria and results of initial testing are presented. The system has been modified for outdoor sampling and is currently being run collocated with a PM-10 dichotomous sampler. Geomet Technologies, Inc., is currently doing side-by-side testing of several indoor and personal samplers including this indoor unit with results to be available by January, 1986.

DESIGN CRITERIA

The impactor was designed to meet several criteria. The primary intended use of the impactor is for the sampling of fine fraction (< 2.5 um) or inhalable fraction (< 10 um) particle sampling in the indoor environment. The flow rate chosen was 4 lpm. The rationale for this flow rate was that it was technically achievable with both battery powered flow controlled pumping systems and line power. This flow rate allows the sampling of about 5.5 m^3 in a day and 40 m^3

in a week. This will facilitate improved accuracy in gravimetric measurements, Beta-gauging operations, and when using XRF automated elemental analysis techniques. Previous studies have indicated that 24 hour indoor home concentrations can range between 5 and 300 ug/m^3 (Spengler, 1981; Ju and Spengler 1981). A flow rate of 4 lpm and minimum concentrations will acheive a mass loading of 25 ug. This is the minimum detectable limit of either the beta-gauge or the gravimetric method with the filter currently used.

The impactor has been designed to use dichotomous sampler type 2" x 2" PTFE membrane filters. Both the rigid mount type (supplied by Membrana, Inc., Ghia Div.) and removable mount type filter slides supplied by Beckman, (42 mm filter disks supplied by Ghia) can be used in the present configuration. An option which will also allow the "Sierra Type" dichotomous filters to be used will be available by 12-1-85. The impactor plates are reusable and have been tested to be adequate for one week sample periods.

UNIFORM DEPOSITION

To utilize automated weighing and analysis procedures which have previously been developed by the US EPA for dichotomous filter samples, a uniform deposition criteria was established (Dzubay and Stevens, 1975). This criteria was defined as the deposit density per CM^2 of the filter shall not exceed 10% of the averaged deposit of filter.

RESULTS

To date, impactor size cut and uniformity of deposition have been characterized by researchers at the Harvard University School of Public Health, the University of Minnesota and the University of Florida. The results of the 2.5 um and 10.0 um Minnesota size cut characteristics tests are presented in Figures 1 and 2. The Minnesota tests were performed with solid particles using fluorescent dyed techniques (Stober and Flachsbart; 1973). The results of the Harvard and University of Florida testing are similar and appear in Figure 3.

Testing for uniform deposition showed the initial plate to filter distance to be inadequate for the 10.0 um nozzles. Lengthening the distance to its present spacing has been shown to meet the uniform deposition criteria for both nozzle sizes. The effect of flow rate on particle cut size has been tested for the 2.5 um impactor. The 50% cut point was determined at 2, 3, 4, 5, and 6 lpm. The results are presented in Figure 4.

Tests were conducted by researchers at Harvard to determine precision estimates for both impactors. Thirty samplers were run in the same environment for two separate 7 day sampling periods. A grand and associated statistics were determined. The results of these tests are presented in Table 1. Using the traditional two standard deviations for precision, the indoor samplers can measure ± 0.7 ug/m^3 and ± 1.5 ug/m^3 respectively.

An experiment was also conducted by Harvard researchers to test the effects of a "rain hat" for outdoor use. Twenty 10.0 um samplers were run outdoors during non-rain days. Ten heads were run with rain hats and ten without for a total of 64.9 hours. As can be seen from these statistics (Table 2), the sampler types agree quite well. The 95% confidence limits are in good agreement.

CONCLUSIONS

The cut points of the impactors have been determined, within experimental error, to be at the original design criteria of 2.5 um and 10.0 um. Precision tests to date have shown the samplers to be well suited for indoor sampling. Limited outdoor testing has shown the impactor and pumping unit to be adaptable to the outdoor environment as well. Preliminary results of the Geomet colocated testing imply that the sampler compares well to other methods.

One hundred samplers have been built to date and deployed for a six month sampling period. Over two hundred pumping units and four hundred impactors will be deployed in November, 1985. To date, these impactors combined with their programmable, flow controlled, quiet sampling unit, have allowed us to reliably collect samples in 280 homes in Watertown, Massachusetts. They will be deployed in St. Louis, Missouri and Kingston/Harriman, Tennessee this fall with similar performance expected.

ACKNOWLEDGEMENTS

The authors wish to thank Ken Robow of the University of Minnesota, Robert Vanderpool of the University of Florida, and Janet Macher, Jack Price, Anthony Majahad and Chan MacVeagh of the Harvard School of Public Health for equipment testing. This work was performed under National Institute of Environmental Health Science Grant NO. ES-01108.

REFERENCES

1. Dzubay, T.G. and Stevens, R.K. Ambient air analysis with dichotomous sampler and x-ray fluorescence spectrometer. Environmental Science & Technology, 9:7, July 1975.

2. Ju, C. and Spengler, J.D. Room-to-Room variations in concentration of respirable particles in residences. Environmental Science & Technology 15(5):595-598, May 1981.

3. Marple, Virgil. Verbal communication to William Turner, April 1985.

4. Speizer, F.E., Bishop, Y. and Ferris, B.G., Jr. An epidemiological approach to the study of the health effects of air pollution. Proceedings of the 4th Symposium on Statistics and the Environment, March 3-5, 1976, Washington, DC pp. 56-68.

5. Spengler, J.D., Dockery, D.W., Turner, W.A., Wolfson, J.M. and Ferris, B.G., Jr. Long-term measurements of respirable sulfates and particles inside and outside homes. Atmospheric Environment 15:23-30, 1981

6. Stober, W. and Flachsbart, H. Evaluation of nebulized ammonium fluorescein as a laboratory aerosol. Atmospheric Environment 7, 1973.

TABLE 1. PRECISION TESTS

	2.5 um ug/m^3	10.0 um ug/m^3
N	28	30
MEAN	9.673	14.693
MEDIAN	9.624	14.836
T MEAN	9.657	14.745
STD. DEV.	0.355	0.762
SE MEAN	0.067	0.139
MAXIMUM	10.662	16.321
MINIMUM	9.114	12.076

TABLE 2. OUTDOOR SAMPLER TESTS 10.0 um (RESULTS IN ug/m^3)

	BOTH	WITH HAT	WITHOUT HAT
N	20	10	10
MEAN	19.39	19.36	19.42
MEDIAN	18.91	18.99	18.82
T MEAN	19.33	19.21	19.31
STD. DEV.	1.72	1.57	1.94
SE MEAN	0.38	0.50	0.61
MAXIMUM	22.96	22.96	22.34
MINIMUM	16.99	16.99	17.41

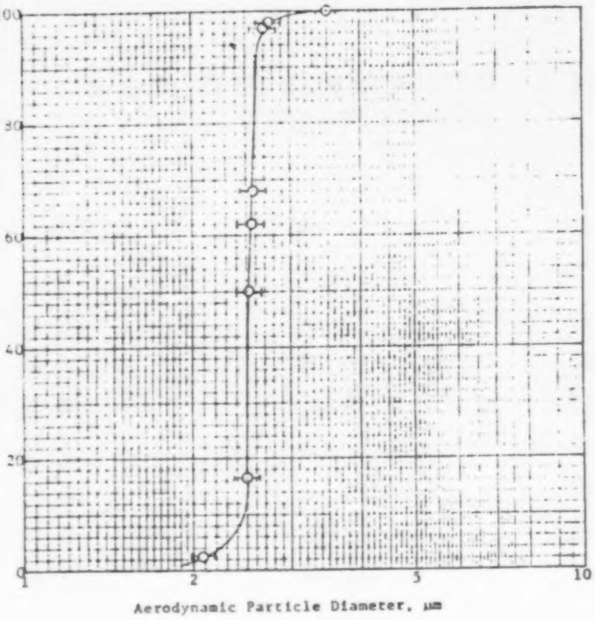


Figure 1. Particle collection efficiency data for final 2.5 µm version (W = 0.0960 inch) at a flow rate of 4 LPM.

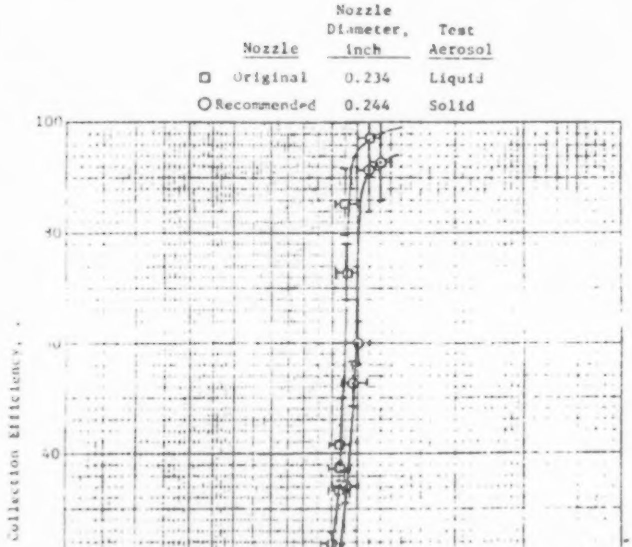


Figure 2. Particle collection efficiency data for original and final 10 µm versions at a flow rate of 4 LPM.

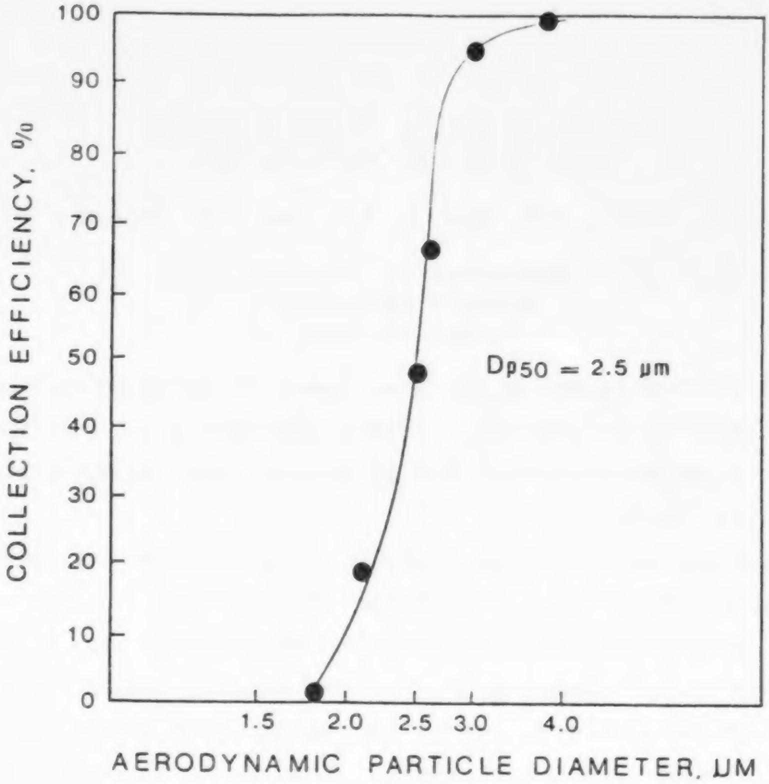


Figure 3. Collection Efficiency Characteristics of the 2.5 Micron Impactor

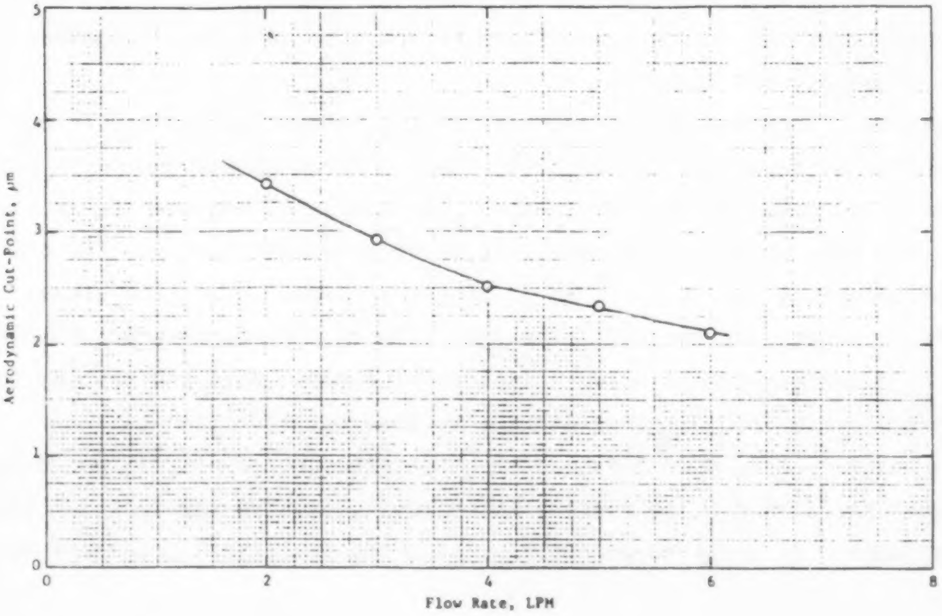


Figure 4. Particle cut-point for [illegible] impactor as a function of flow rate.

ANALYSIS OF NITRITE IN NO_2 DIFFUSION TUBES USING ION CHROMATOGRAPHY

D.P. Miller, K.C. McGill, H.S. Lam, T.L. Shields

Department of Chemistry
Washburn University
Topeka, KS 66621

The subject of this report is the development of an analytical method to analyze Palmes Tubes for nitrite ion. Palmes Tubes are passive diffusion controlled samplers for nitrogen dioxide in the atmosphere, and the NO_2 collected is analyzed as nitrite ion(1).

Passive samplers for trace components in the atmosphere are inexpensive to fabricate and deploy, and as a result they are utilized in large numbers when it is necessary to determine the time average concentration over a large spacial area. An additional advantage is that most passive samplers are small in size, and when carried around by people, they measure the concentration in the particular spacial area occupied by people. As a result of large numbers of samples obtained from large numbers of identical exposure situations, passive devices often give the most accurate indication of human exposure to a particular trace component.

Palmes tubes have been used for about ten years in numerous studies by different research groups. In addition, they also have been subjected to a number of laboratory studies. As a result, workers today are familiar with the capabilities and limitations of the Palmes Tube, and how it behaves in a variety of exposure situations.

The traditional method of analysis of the Palmes Tube is spectrophotometric. Triethanolamine deposited on stainless steel screens absorb the nitrogen dioxide, which is converted to nitrite ion. For analysis, the nitrite is used to make an azo dye, which is then measured spectrophotometrically. The practical limit of detection is 7×10^{-10} moles of nitrite ion. Using the dimensions of the diffusion path and the diffusion coefficient, this corresponds to 300 ppb hr of collected nitrogen dioxide. Typically, Palmes Tubes are exposed for one week to collect enough nitrogen dioxide to give reliable results.

In order to gain more information about exposure levels, it would be useful to measure nitrogen dioxide concentrations using passive samplers for times shorter than one week. In order to accomplish this, the analytical procedure needs more sensitivity and remain free from interferences. One approach, presented here, uses a slightly modified Palmes Tube to collect the nitrogen dioxide, and ion chromatography as the analytical method.

The traditional Palmes Tube is assembled from a cylindrical acrylic tube, and a 1/2 inch CAPLUG which fits over one end and contains three stainless steel screens. The tube was modified in order to minimize contamination caused by handling, and to facilitate the analytical procedure. The modification consists of a Teflon plug pressed into a stainless steel ring and forced inside the CAPLUG. A stainless steel screen is pressed into a depression in the Teflon. The inside edge of the acrylic tube is beveled to prevent the end of the acrylic tube from touching the screen when the tube is assembled, which would cause unacceptable chloride contamination during handling of the unassembled tube parts.

The inside of the CAPLUG with the screen is squirted with a stream of deionized water, the excess water is removed by centrifugal force in a mechanical spinner, and then set on paper towels. Using a micropippete, 20 microliters of a solution of deionized water and triethanolamine is deposited on each screen, and then the CAPLUG is placed immediately inside a long glass tube in which NO_2 free air continuously flows. The screen are coated with 3 x 10^{-6} mole of triethanolamine. The batch of treated CAPLUGs are allowed to dry in the tube. If left inside the drying tube too long, the screens will pick up unacceptable amounts of NO_2, since the last traces of NO_2 are difficult to remove from the air stream. The CAPLUGs are removed from the drying apparatus, placed on the beveled end of the acrylic tubes with an empty CAPLUG closing the other end of the tube. The assembled tube is then placed inside a shipping container, which is a friction top metal can. Before the container is closed, a polystyrene coffee cup stuffed with a crumpled paper towel moistened with triethanolamine is placed inside the container to scavenge any nitrogen dioxide.

The tubes appear externally identical to the traditional Palmes Tubes, and are handled and exposed in the field in the traditional manner.

For analysis, because of the small amount of nitrite ion present on the screens, the entire sample must be transfered and trapped in a concentrator column. The two problems associated with this task is avoiding chloride contamination and preventing air bubbles from entering the chromatograph, which are resolved by using a transfer apparatus. The CAPLUG with the screen is removed from the acrylic tube and fit over the open end of the transfer apparatus, and clamped tight. The appartus consists of Teflon surrounded by a metal housing. The stainless steel ring inside the CAPLUG and the metal housing are required to prevent the Teflon from distorting under pressure. Two Tefzel tubes enter the bottom of the apparatus, one ending at the bottom of a cavity, the other extending almost to the top of the cavity but not touching the screen. The cavity is filled with deionized water from the bottom tubing until it flows out the extended tubing, without touching the screen. The deionized water flow is then reversed, and ten milliliters are forced through the apparatus using a Milton Roy MiniPump. What air remaining inside the apparatus is compressed to a tiny bubble and does not leave. The force of the water squirting on the screen rinses all the nitrite out and transfers it to the concentrator column. After the transfer, the cavity is filled with clean air before unclamping and removing the CAPLUG. The CAPLUG is removed, and the apparatus is ready to receive the next sample.

The concentrator column with the trapped sample is switched into the eluent stream of the ion chromatograph in the usual manner, to complete the analysis.

The ion chromatograph used in this work is a Dionex 2010i, with a TAC-1 concentrator column, an anion guard column, an AS3 analytical column, an AFS-1 fiber suppressor, a conductivity detector, and a SP4270 integrator/recorder. The eluent was .0588 grams $NaHCO_3$ and .2333 grams Na_2CO_3 in one liter of deionized water.

The chromatogram takes about 12 minutes from inject to sulfate. The order of the first peaks are: waterdip, fluoride, chloride, nitrite. Between the nitrite and the sulfate peaks, the concentrator column is switched out and loaded with the next sample, so that with this configuration one sample is run every 12 minutes.

The nitrite appears on the rising shoulder of the waterdip, and at the 0.3 μs level required by the small amount of nitrite in each sample, the signal out of the detector is negative. The SP4270 integrator cannot accept negative signals, and the detector does not have a manual offset. To observe the nitrite peaks in the waterdip, a battery driven voltage divider was added in series to the output of the detector which provided a positive voltage offset to the signal.

The instrument was checked for linearity by spiking the screen in a CAPLUG with known amounts of nitrite. The blank screens would typically give no detectable peak or a just detectable peak, about three times the baseline noise, which corresponded to 1×10^{-11} mole nitrite. Peak heights were used throughout these preliminary runs. The instrument was linear from 10^{-11} through 10^{-7} mole nitrite, and nonlinear at 10^{-6} mole. A typical trial consisting of 7 runs at 2×10^{-10} mole of nitrite gave peaks heights of 0.081 μS with an average deviation of 0.002 μS.

Replicate sets of ambient exposures were run to test precision and reveal possible interferences. A typical run consisted of five tubes total, two blanks and three replicate samples. All five were carried clipped to a shirt pocket for 18 hours. The blanks gave 4 ppb hr, and the three replicates gave 80 ppb hr with an average deviation of 3 ppb hr. None of the ambient test runs had serious chloride contamination problems, including replicate sets left exposed in the laboratory, representing a worst case situation due to the presence of hydrochloric acid.

Controlled exposure in test chambers are in progress, in order to determine the accuracy, and the results will be published when this work has been completed.

The operating costs associated with this method of analyzing Palmes Tubes can be approximated as follows: The modified Palmes Tubes, since they contain about twice as many components, will cost about twice as much as a conventional Palmes Tube. The other front end cost is the ion chromatograph, the transfer apparatus, and the source of deionized water. The transfer apparatus is not available commercially, and includes several valves, Teflon lines, a Milton Roy MiniPump, and a part machined from Teflon and metal which fits in a clamping device. The transfer apparatus would be straight forward to automate, if desired.

The time required to prepare the tubes is about the same as for the conventional Palmes Tubes. The analysis time on a manual single channel instrument using the present eluent and analytical column is 12 minutes per sample. The limiting factor is the length of time to elude the sulfate peak, which if present, would disturb the base line of a subsequent chromatogram if the next sample were injected immediately after the nitrite peak. In addition to the time per sample, calibration and QA samples are required.

A major consideration under operating costs is that the instrument must be dedicated full time to the Palmes Tube analysis. Starting from scratch, it takes the better part of a week to eliminate contamination problems at the 10^{-11} mole level of detection. After an extended shut down of several days, it takes most of a day for the instrument to settle down, while an overnight shut down requires a couple of hours. As a result, the hidden operating costs of start up time greatly exceeds actual running time for the analysis of an occasional small batch of samples.

REFERENCES

1. Palmes, E.D., Gunnison, A.F., DiMattiok J., and Tomezyk, C. (1976) Personal Samples for Nitrogen Dioxide. Am. Ind. Hyg. Assoc. J. 37, 570-577.

EVALUATION OF COED-1 PORTABLE CARBON MONOXIDE PERSONAL EXPOSURE MONITORS

by

C.F. Turlington, J.K. Bostick, C.W. Abel,
C.G. Weant, and J.C. Holland
Northrop Services, Inc. – Environmental Sciences
P.O. Box 12313
Research Triangle Park, NC 27709

The instrument evaluations in this report were performed in support of studies of human exposure to carbon monoxide (CO). A General Electric (GE) CO monitor was selected by EPA. Microprocessors were purchased from Magus Group and Hewlett-Packard. Rockwell International assembled the monitors and microprocessors into field instruments identified as CO exposure dosimeters, Model COED-1. Northrop Services, Inc. – Environmental Sciences provided independent acceptance and performance testing of the monitors.

Over 700 tests have been performed on 104 GE CO monitors at various times during modification and service. The COED-1 modifications caused no changes in the performance of the analyzers. Testing of 21 COED-1 units after field studies revealed a cell half-life of between one and two years. Temperature sensitivity is the sign of cell degradation. Other tests at room temperature do not indicate cell degradation. The COED-1's gas flow system limits performance if not maintained. Out of the 21 returned units tested, 38% required attention. No change in linearity or data storage was observed after field use. All tests of analyzer linearity or of Magus data systems have been successful. The data systems have failed only when electrical power has failed. Some nonlinear performance below 20 ppm was observed in the field. Since only one value below 20 ppm was measured, the acceptance linearity tests did not clearly indicate this problem.

INTRODUCTION

The instrument evaluations reported herein were performed in support of studies of human exposure to carbon monoxide (CO). The primary objectives of these studies were to validate a methodology for measuring the distribution of CO exposures in a representative sample of an urban population and to estimate the risk to the entire population. Other goals of the studies included relating the exposure estimate to fixed site measurements (both indoor and outdoor) and developing a method for selecting and measuring microenvironments where significant human exposures occur. Carbon monoxide was chosen because its sources are known, its health effects are well characterized, and instruments are available. Portable detectors for CO have been developed by several companies; however, they are generally designed for industrial or mining applications and lack operational features or CO concentration ranges suitable for ambient field studies. Therefore, a commercially available system with a satisfactory range was modified to provide the necessary operational features required for ambient monitoring.

An existing industrial CO monitor, the General Electric (GE) direct reading SPE CO detector, Model 15ECS3CO3 (CO3), was selected by EPA for these studies. This unit was readily available and provided real time data in the desired CO concentration range, but lacked data logging, integrating, and timing capabilities. A microprocessor-based control package was purchased from Magus Group, Inc., to provide the data handling and control, and Rockwell International assembled the components into a working monitor identified as the CO exposure dosimeter, Model COED-1.

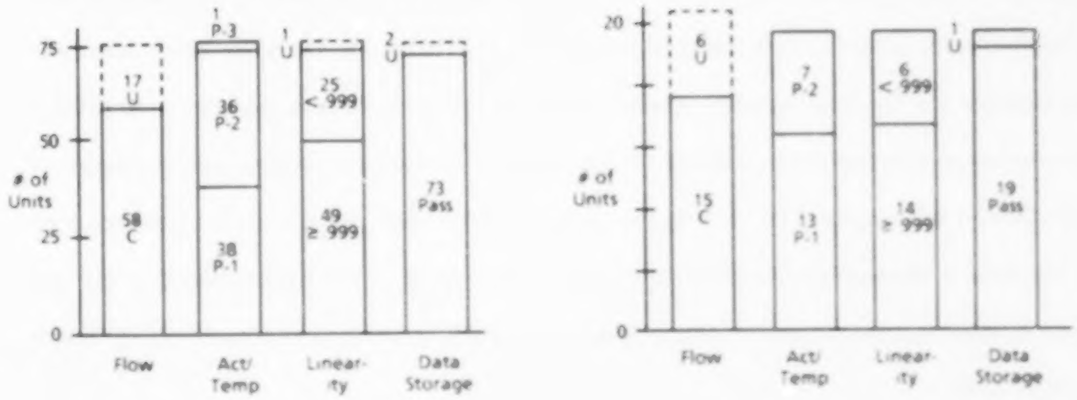
Northrop Services, Inc. – Environmental Sciences' (NSI-ES) role in these studies was coordination and testing of the monitors as they progressed through the phases of construction and use. Performance tests of the GE units were necessary to satisfy warranty requirements, while the completed units from Rockwell had to undergo an additional test and evaluation phase because of the changes. Final testing was conducted after the field studies to determine any performance degradation over the study period.

The initial test phase consisted of a series of performance checks of the CO3 units over the temperature range 5-40°C. Defective units were identified and shipped back to the manufacturer. The modified units, COED-1s, were subjected to a similar series of tests to verify the correct operation of the detector and the data handling system. When all test requirements were met, the COED-1 units were released for use in the ambient CO field studies. Primary field studies were conducted in Denver, CO and Washington, D.C., during the winter of 1982-1983. After the units were returned from the field, a representative sample of the units was tested. This report describes the test procedures used, reports the results, and provides conclusions concerning improvements for future use of the COED-1.

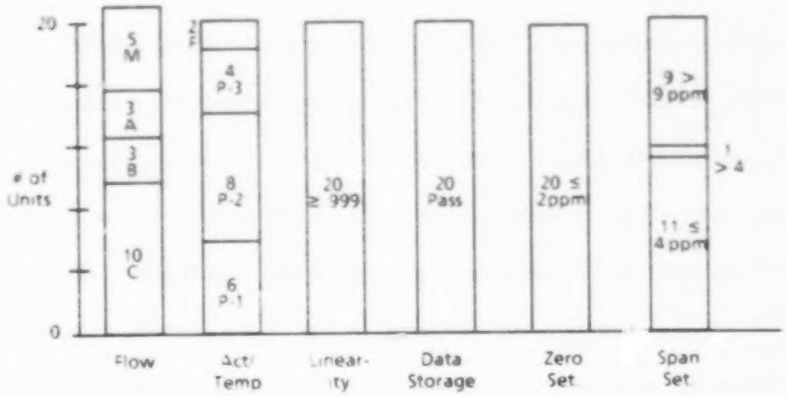
CONCLUSIONS and RECOMMENDATIONS

Over 700 tests were performed on 104 monitors at various times during their modification and service life. The COED-1 modifications caused no changes in the performance of the analyzers. The results of the COED-1 evaluations are summarized in Figure 1. Each bar consists of two to four blocks, ranging from the best working units in the bottom block to the worst or untested units in the top block. Each block contains the number of monitors in that classification and their performance indicator. The performance indicators are explained by the figure caption. Figure 1A pictures the performance of the entire population of 75 COED-1 analyzers before field testing. Figure 1B, illustrating the performance of 20 units before they were sent to the field, may be compared with Figure 1C, showing the performance of those same monitors after they were returned from field sites. This comparison shows no change in linearity or data storage; all 20 units did as well or better after field use. The zero settings as-received from the field were fairly close to the correct values, considering the time and distance of shipping since the monitors were set. Most of the span errors indicated a systematic deviation discussed in detail below. The two areas in which performance worsened were the flow rates and temperature ranges. The flow problems were corrected by maintenance on the pumps and filters.

A. All 75 COED-1 Units Before Field Use. **B. Selected Units Before Field Use.**



C. Selected Units After Field Use.



The number in each block is the number of units; the letter indicates the performance of those units according to the following key:

A- Adjusted pump voltage up and back to start, then O.K.
B- Bubble meter flow passes as-received; mass flow meter restricts.
C- Mass flow meter reading passes test.
F- Failed activation.
M- Maintenance required to pass flow test.
P- Passes activation test:
  1. 5° to 40°C temperature range
  2. 10° to 30°C temperature range
  3. narrower than 10° to 30°C temperature range
U- Untested; but probably O.K. since 5 out of 6 initially untested units produced a B or C when returned from the field, and no unit has ever failed the data storage test.

Figure 1. Summary Performance Charts.

The temperature range degradation is of most concern because its correction requires replacement of the cell, an activation period, and retesting. After the field studies, 30% of the 20 units had degraded to the point that they no longer met the acceptance criteria. Degradation with time is more evident when the date of cell installation is considered. Three of the units had their cells replaced and were retested shortly before field use. These units performed as well or better upon their return, while 57% of the older units failed. If data were available for the number of hours of use for each unit, this could be compared with the cell exposure to water and electrical potential and with the performance to determine whether use increased the degradation. Since the cells remain moist and have a potential constantly applied to them, their age and ambient storage conditions probably are the dominant factors in cell degradation, but heavy use may hasten the process. Temperature sensitivity and irreproducible behavior are the signs of cell degradation. These indicators should be checked, or cells automatically replaced, every 9-12 months. Other tests such as linearity, daily zero and span checks, and flow do not indicate cell degradation.

The monitor's gas flow system can also limit performance if not maintained. In addition to the initial flow and pump voltage checks on all units, the pump motor resistance or impedance should be measured to eliminate pumps that drain batteries too rapidly. More attention to the monitor's gas flow system in the field is needed, as 24% of the sample of returned units required service, and 14% required minor adjustments to achieve proper flow. A good daily and weekly maintenance program could reduce flow failures, but the greatest improvement in flow system reliability would be, as suggested by Jungers and Johnson, to invert the flow through the filter-scrubber tube. This design change would improve reliability and greatly reduce flow system maintenance.

No change in the linearity and data storage performance was observed. The data systems have failed only when electrical power or connections have failed. Generally, such failures were obvious and prevented testing; therefore, all completed tests of linearity or data systems performance have been successful. Only one unit out of 21 sampled from the field had a bad electrical connection preventing it from being tested. Another unit had batteries that would not charge, but it passed when fresh cells were installed. Although unreliable power and electronic problems were experienced in the field, they were not observed during acceptance testing. The field problems may have been due to a combination of weather conditions, physical shock, and vibration.

Nonlinear performance below 20 ppm was observed in the field for some analyzers. The acceptance linearity tests did not clearly indicate this problem since only one value below 20 ppm was measured. To identify this nonlinearity, the data logging and linearity tests should be combined with all measurements stored by the data system and more concentrations measured between 0 and 20 ppm. The nonlinearity problem probably was reduced for some Washington, D.C. field data by offsetting the zero reading to 1 ppm. Nonlinearity was mitigated in Denver by balancing the detector output to the data system input.

The performance data for the units tested after the field studies were separated into groups by age, former field site, and performance test. Means and standard deviations were computed for each category, and a statistical test was applied to each pair of means to determine if they differed with better than 95% probability. The only statistically significant deviation was the high span readings found on the units used in Denver. The high span readings were not explained by theoretical corrections for flow deviations and the difference in mean barometric pressure between Denver and NC. Theoretical corrections may be in error, or a systematic error in the calibration method may exist. Closer attention must be given to this deviation if testing continues at high altitudes.

BIBLIOGRAPHY

Bay, H.W., K.F. Blurton, J.M. Sedlak, and A.M. Valentine. 1974. Electrochemical technique for the measurement of carbon monoxide. *Anal. Chem.* 46:1837-1839.

Hoel, P.G. 1966. Introduction to mathematical statistics. John Wiley & Sons, NY.

Jungers, R.H. and T. Johnson. Quality assurance planning and implementation for the Denver carbon monoxide study. Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC.

Kosek, J.A. and A.H. Gruber. 1981. Development of improved detection instruments for toxic gas contaminants in mining atmospheres. [Contract #H0395132 (no report #)] Bureau of Mines, Washington, D.C.

LaConti, A.B., M.E. Nolan, J.A. Kosek, and J.M. Sedlak. 1980. Recent developments in electrochemical SPE sensor cells for measuring CO and oxides of nitrogen. In: ACS Symposium Ser. No. 149, pp. 551-573.

Turlington, C.F., J.K. Bostick, C.W. Abel, C.G. Weant, and J.C. Holland. Submitted. Evaluation of COED-1 and COED-2 portable carbon monoxide personal exposure moitors. TN-84-02. Research Triangle Park, NC: Northrop Services, Inc. – Environmental Sciences.

MONITORING OF BENZENE IN AMBIENT AIR WITH ORGANIC VAPOR BADGES

Kochy K. Fung and Barbara J. Wright
Environmental Research & Technology, Inc.
Newbury Park, CA 91320

INTRODUCTION

Benzene is a toxic substance commonly found in ambient air, especially in the urban environment. Benzene is an industrial solvent and is also a component of gasoline, typically present in concentrations of one to two percent. Evaporative emissions account for some of the benzene in ambient air. However, benzene can also be produced in combustion processes including those in automobiles and can be emitted with the exhaust into the environment. Recently, the California Air Resources Board (CARB) has identified benzene as the first pollutant to be controlled under its toxic air contaminant control program. Thus, there is a need for an accurate, reliable, low-cost technique for the routine monitoring of benzene.

The most common method of sampling for benzene is by adsorption on charcoal tubes (NIOSH, 1977). Air is drawn through the tube at a known flow rate using a pump. At the completion of sampling, the benzene adsorbed by the charcoal is eluted with a solvent and determined by gas chromatography. Tedlar (polyvinyl fluoride) bags and metal canisters have also been used for benzene sampling (Singh, 1980; Grosjean and Fung, 1984). A grabbed or integrated air sample is pumped into the bag or canister and brought back to the laboratory where the hydrocarbons in the sample, including benzene, are determined with gas chromatography after cryogenic sample preconcentration. Benzene has also been monitored successfully using an on-site gas chromatograph equipped with a photoionization detector (Hester, 1979).

While these techniques will yield reliable benzene data, their application to large-scale field monitoring may be costly. Equipment costs, maintenance and flow calibrations all make such programs more expensive. Availability of power, sampler noise, and equipment security are major problems in some monitoring situations. The advent of the passive monitor (badge) has resolved a lot of these difficulties. This commercially-available device is inexpensive, lightweight for easy placement and handling, and requires no associated sampling equipment. It has been used routinely as a personnel monitor in industrial hygiene applications in place of the charcoal tube/pump method. Thus, there has been a great deal of interest in determining whether the badge could be applied to the monitoring of ambient levels of benzene at concentrations several hundred times lower than the concentrations the device was originally meant to collect. A study was conducted in which data from the badge samples was intercompared with data from charcoal tube and Tedlar bag samples. Benzene levels were measured side by side using these three techniques at the perimeter and center of two gasoline stations, in the vicininty of a bulk terminal, and adjacent to a busy freeway in southern California.

EXPERIMENTAL

The organic vapor badges were obtained from duPont. Type GAA contains one strip of charcoal, and type GBB is similar with an additional backup strip of charcoal. Type GBB was used primarily because it was not known if breakthrough would occur, and the backup provided assurance that none had occurred during sampling. The badges were hung on posts and allowed to sample for 24 hours instead of shorter durations since the sampling rate of the badges for benzene is 35.6 ccpm. The charcoal tubes were SKC sorbent tubes with 400 and 200 mg of charcoal in a front and backup section, respectively. AC-powered sampling pumps were used to pull air at 1 lpm through the tubes which were placed adjacent to the badges on the posts. The Tedlar bags were 50-liter capacity. They were on loan for the study by CARB. The bag samplers were designed to be comparable to those used by the CARB. Filtered ambient air was pushed through a pressure regulator, relief valve and rotameter into the bag at approximately 35 ccpm for 24 hours. The air inlet tube to the pump was also located next to the badges and tubes so that all devices sampled the same air parcel. After sampling, the badges were covered and sealed inside foil bags provided by the manufacturer; the charcoal tube ends were closed with cap plugs, and the bag inlet was sealed with a cap nut for transporting back to the laboratory.

Meteorological data such as wind speed, wind direction and temperature were recorded on strip charts using two MRI mechanical weather stations, one located at the upwind perimeter, and the other downwind. The percent relative humidity was measured with a sling psychrometer whose thermometers had been compared to an NBS thermometer.

Within 24 hours of collection, the bag samples were analyzed with high resolution capillary gas chromatography after cryogenic sample preconcentration

(3). All the tubes and badges were stored in a freezer upon return to the laboratory until they were to be analyzed. They were extracted with benzene-free carbon disulfide (CS_2) and analyzed using packed column gas chromatography with flame ionization detection.

RESULTS AND DISCUSSION

The 24-hour average benzene concentrations measured at the four locations are summarized in Table 1. The results showed that the benzene levels determined using the three different techniques were equivalent. The mean benzene concentrations derived from the entire data set are 5.3 ± 1.3, 5.7 ± 1.4, and 6.1 ± 1.4 ppb, respectively for the badge, tube and bag method. It is clear that the differences observed amongst the three are statistically insignificant.

The CS_2 was Fisher "purified" reagent grade, yet it contained considerable quantities of benzene. For example, the CS_2 contained 14 µg/ml of benzene compared with typical benzene samples which ranged from 4 to 22 µg/ml. This contaminated CS_2 was worthless for direct use in this study. Thus, a method for purifying the CS_2 was developed. The solvent was acid distilled, and only the benzene-free cuts of the distillate were used in the analyses.

There has been concern regarding the effect of high humidity on sample collection by the badge. In general, higher humidity tends to reduce the adsorption capacity of the charcoal. For both the GAA (single strip) and GBB (double strip) badges, duPont has rated their capacity for benzene to be greater than 12 hours while sampling at 10 ppm and 80% relative humidity. In the present application, the benzene levels were over a thousand times lower, and the relative humidity ranged from 22% to 93%. High humidity was experienced during the night and early morning hours. Analysis of the backup strips showed that breakthrough had not occurred with any of the badges used.

Since benzene was not detectable in the field blanks, the analytical detection limit dictated the lower quantifiable limit (LQL) of the badge. The LQL has been estimated to be 0.3 ppbv based on a signal-to-noise ratio of two with the present sampling and analytical conditions.

In conclusion, the badge appears to be useful for monitoring ambient levels of benzene. Humidity was not a problem in causing breakthrough. Significant

TABLE 1

AMBIENT BENZENE LEVELS MEASURED AT FOUR LOCATIONS IN SOUTHERN CALIFORNIA

		24-Hour Average Benzene, ppb		
Site	Post No.	Badge	Tube	Bag
I	1	5.8 ± 0.3*	6.4	6.6
	4	7.6	6.8	
	5	6.0	5.6 ± 0.6*	7.4
	6	7.0	6.0	
	9	6.2 ± 0.1*	7.0	
II	2	5.7	6.2	7.7
	4	6.5	4.9	
	5	5.3	9.2	
	6	4.9	5.0	6.4
	7	4.5	4.5	
III	2	3.7 ± 0.5*	4.0	4.2 ± 0.1*
	3	4.1 ± 0.2*	4.5 ± 0.4*	
	4	3.6 ± 0.5*	4.1	
IV	2	5.6 ± 0.1*	6.7	6.0
	6	3.5 ± 0.1*	4.1	4.3 ± 0.3*

---

*Average of duplicate or triplicate samples.

improvement in LQL can be expected if capillary gas chromatography is used for the analysis.

REFERENCES

1. Grosjean, D. and K. Fung, 1984. "Hydrocarbons and Carbonyls in Los Angeles Air." JAPCA, 34: 537.

2. Hester, N.E. and R.A. Meyer, 1979. " A Sensitive Technique for Measurement of Benzene and Alkylbenzenes in Air." Env. Sci. Technol., 13: 107.

3. National Isntitute for Occupational Safety and Health P & CAM No. 127, 1977. "Organic Solvents in Air."

4. Singh, H.B., 1980. "Guidance for the Collection and Use of Ambient Hydrocarbon Species Data in Development of Ozone Control Strategies." U.S. Environmental Protection Agency Report. EPA-450/4-80-008, Office of Air Quality Planning and Standards, Research Triangle Park, NC, April.

A PASSIVE DOSIMETRY METHOD FOR DETERMINING HYDRAZINE IN AIR

Susan L. Rose and Jeffrey R. Wyatt
Naval Research Laboratory
Chemistry Division
Washington, D.C. 20375-5000

Chester M. Hawkins
Geo-Centers, Inc.
Suitland, MD 20746

INTRODUCTION

Large quantities of monomethylhydrazine (MMH) and hydrazine are used as high energy propellants in the space shuttle. Because MMH and hydrazine are suspected carcinogens, NASA must be concerned about the toxicological problems that could arise as a result of fuel storage and handling operations. Consequently Kennedy Space Center has established special guidelines for maintaining personnel safety; which include routine air monitoring to ensure that exposure to MMH and hydrazine does not exceed the American Conference of Governmental Industrial Hygienists (ACGIH) recommended threshold limit values (TLV) of 200 and 100 parts-per-billion (ppb) for MMH and hydrazine, respectively.

NASA has a need for inexpensive, quantitative personal dosimeters that could be distributed to a large number of personnel. The badge should be worn for at least one week and could be monitored in the event of a hydrazine spill. In addition, a portion of the dosimeters would be analyzed regularly to provide average exposure levels.

The development of a dosimeter badge is complicated by the reactivity of the hydrazines. Hydrazines have a strong tendency to absorb and decompose on surfaces, particularly metals, making them difficult to sample and measure. Since they are polar, reactive compounds, they associate with water vapor, form aerosols, are sensitive to air oxidation and react readily with carbon dioxide.

Few commercial detectors or acceptable techniques are available. A passive electrochemical monitor was tested and found to be unreliable. Liquid-sorbent badges were investigated, but lacked the precision necessary. Strong acids on solid supports have been used for field sampling of hydrazine, but MMH is not stable in this medium. Antioxidants have improved the stability of MMH solutions, therefore we decided to investigate a solid support coated with an organic acid with antioxidant properties, citric acid.

EXPERIMENTAL

The passive dosimeter shown in figure 1 has been developed and is being evaluated. A plastic sample holder, 1/2" deep and 1 3/4" in diameter, supports the collection substrate. The collector is a disc of polyester matted drafting paper that is dipped in 20% citric acid in methanol solution and allowed to dry. A 1/16" spacer provides an air gap between the substrate and the top of the badge. Passive diffusion is controlled by a one inch diameter pattern of holes.

The dosimeter badges are being tested in the glass and Teflon constructed test apparatus shown in figure 2. Diffusion tubes provide reproducible hydrazine vapors that are easily varied. Hydrazine contaminated air flows into the dosimeter test (figure 3) chamber at 10 liters/min. Teflon baffles are used to improve laminar flow through the chamber. At least two hours are allowed for equilibration between changes in experimental conditions, and the concentration is verified by collecting impinger samples from the chamber with analysis by colorimetric and coulometric methods. Three chambers of different diameters allow face velocity tests without changes in the gas stream conditions.

The badges are being analyzed using two accepted wet chemical methods: (1) A NIOSH approved method (#S149) using phosphomolybdic acid, and (2) a coulometric titration with bromide and amperometric endpoint detection.

RESULTS

The precision of the dosimeter was tested by exposing the badges to a dry gas stream contaminated with 242 ppb MMH and measuring the amount of MMH detected versus the exposure time. Exposure times between 5 and 65 hours were examined over several days. A correlation coefficient of 0.996 was obtained for 107 data points. The badge sample rate was calculated from this data and found to be 31 ml/min. The stability was verified in two tests. In each test, four badges were exposed to MMH, two of the badge substrates were analyzed immediately and the other two substrates were stored in the dark at room temperature in a sealed container. No degraduation was observed for any of the storage periods (3-7 days). The linearity was investigated by exposing the badges to MMH between 70 and 240 ppb in dry air for 16 hours. Deviations from ideal performance were observed below 100 ppb. Because we suspected adsorption as the problem, the adsorption of the hydrazine on the badge at low concentrations or low exposure time was investigated by constructing the badge from three different materials: (1) machined Teflon, (2) machined polypropylene, and (3) molded Fluoroware. The badges were exposed to MMH at the TLV in both dry and humid air from 15 minutes to 16 hours. The apparent sample rate was calculated by comparing the moles of hydrazine collected with the actual concentration. The apparent sample rate was reduced for all of the badges compared to the calculated sample rate. The machined Teflon and polypropylene badges were much worse than the molded plastic, particularly in humid air. The apparent sample rate is 75% of the calculated sample rate sample for the molded plastic badges at approximately one hour. Therefore, the molded plastic was used for the remainder of the tests. The relative humidity effects were tested using MMH at the TLV, a face velocity of 5 ft/min and relative humidities between 10-75% RH. Minimal effects on the performance were observed. The face velocity affects on the sample rate were also tested for 2, 5 and 20 ft/min. No significant variations in the amount of MMH collected were observed. Interference by isopropyl alcohol, ammonia, NO_2, and freons were examined by mixing TLV levels of each with TLV levels of MMH. Little variation was observed in the MMH concentration in the badge compared to analyzed impinger samples from the same gas stream.

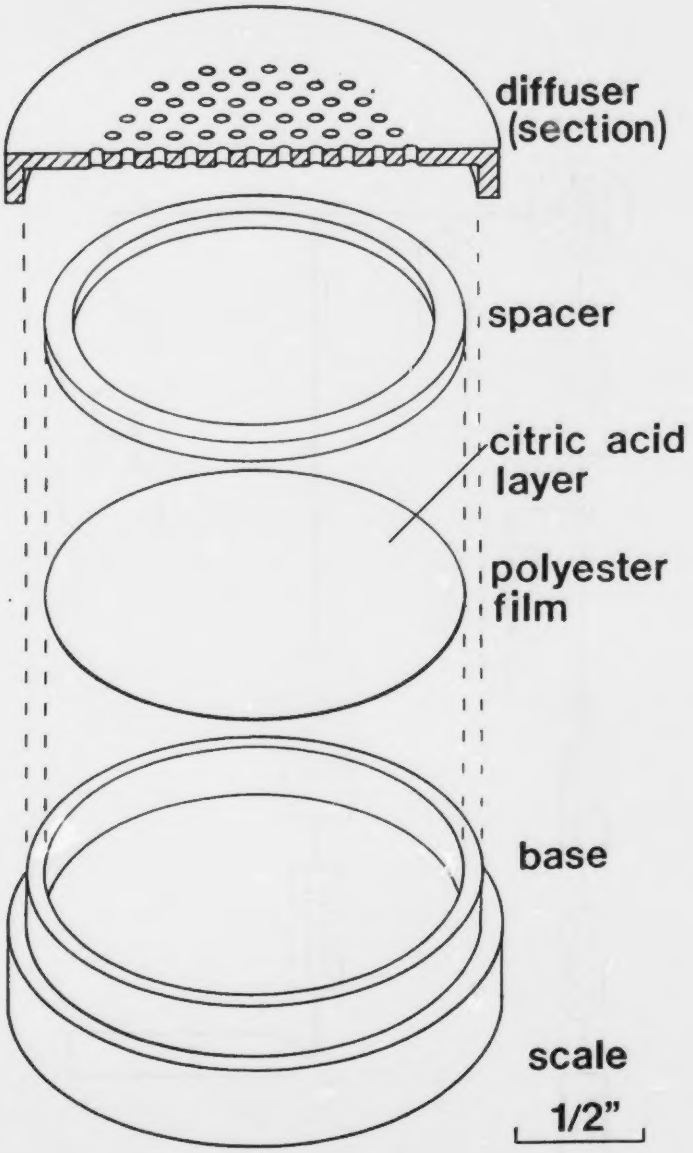

diffuser (section)
spacer
citric acid layer
polyester film
base
scale
1/2"

Figure 1. Dosimeter

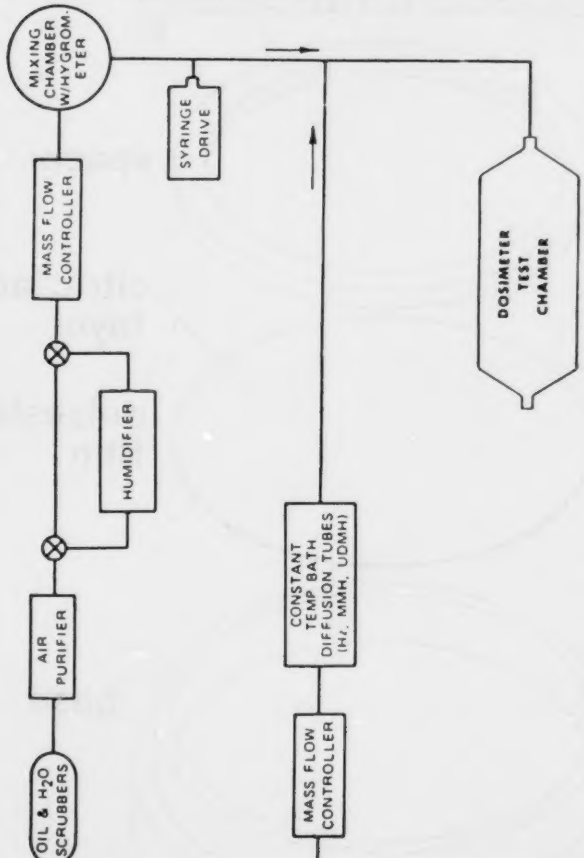

HOUSE AIR
OIL & H_2O SCRUBBERS
AIR PURIFIER
HUMIDIFIER
MASS FLOW CONTROLLER
MIXING CHAMBER W/HYGROMETER
SYRINGE DRIVE
DOSIMETER TEST CHAMBER
N_2
MASS FLOW CONTROLLER
CONSTANT TEMP BATH DIFFUSION TUBES (HZ, MMH, UDMH)

Figure 2. Test Apparatus

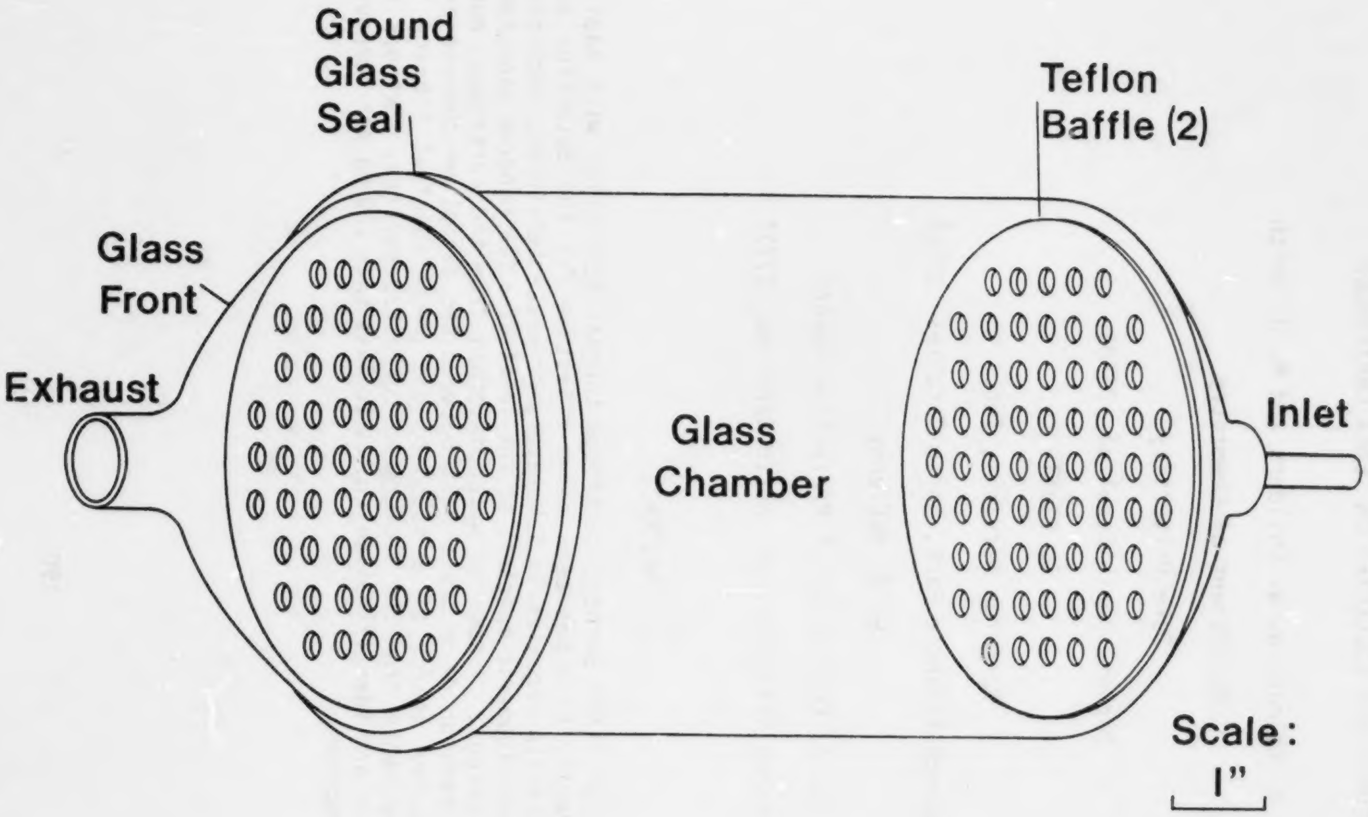

Ground
Glass
Seal
Teflon
Baffle (2)
Glass
Front
Exhaust
Glass
Chamber
Inlet
Scale:
1"

Figure 3. Dosimeter Test Chamber

GC/FTIR STUDIES OF VOLATILE ORGANIC COMPOUNDS COLLECTED ON TENAX CARTRIDGES

R. A. Palmer, J. W. Childers and M. J. Smith
Department of Chemistry
Duke University
Durham, North Carolina 27706
J. D. Pleil
Northrop Services, Inc.
Research Triangle Park, North Carolina 27711
W. A. McClenny
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

ABSTRACT

The combination of TENAX sorbent cartridge thermal desorption with capillary column GC/on-the-fly FTIR has been shown effective for the detection and identification of volatile organics in laboratory-generated mixtures, including the distinction between isomeric species, at the level of a few hundred nanograms per compound per cartridge. Traces of water desorbed from the cartridges must be reduced by the insertion of a dryer unit between the desoption chamber and the GC column. Computer search of a standard gas phase spectral library is used to identify components from the background corrected spectra. Methods of lowering the detection and identification limits to less than 100 ng per compound per cartridge are proposed.

INTRODUCTION

Gas chromatography combined with Fourier transform infrared spectroscopy is an efffective means of detecting and identifying volatile organics found in ambient air samples and provides structural information that is complementary to GC/mass spectroscopic techniques. While GC/MS is more sensitive than on-the-fly GC/FTIR, it often lacks the ability to distinguish unambiguously between geometrical isomers. GC/FTIR, on the other hand, can be used to make a positive distinction between isomeric compounds based on their unique infrared spectra.[1,2,3] In addition, when combined with retention time data, GC/FTIR can also be used for independent unequivocal identification of trace organics in many cases. However, since GC/FTIR lacks the sensitivity to detect trace organic pollutants at ambient air concentrations, some method of preconcentrating the samples is required. Collection on sorbent cartridges followed by thermal desorption would appear to be a viable solution to this problem. In this study the feasibility of the use of TENAX-GC cartridge thermal desorption combined with subsequent cryotrapping[5,6] has been evaluated as a delivery system for on-the-fly GC/FTIR detection and identification of selected organic compounds. Special emphasis has been given to the identification of geometrical isomers. Instrumental problems addressed include removal of interferences due to co-eluting water, spectral cleanup to facilitate library based identifications, and development of an analytical method to coordinate the various instrument subsystems necessary for precise analyses.

EXPERIMENTAL

CHEMICALS

Samples were prepared by the Northrop Services, Inc. (NSI) Volatile Organics Standards Laboratory. Neat compounds (5 to 10 µL amounts) were injected into 2L static dilution bottles filled with zero grade helium. The resulting gas mixtures were equilibrated for a minimum of one hour at 65°C. Syringe samples of the mixture were analyzed by capillary GC and referenced to diffusion tube standards that were certified by time dependent weight loss rates. This established accurate concentration values (typically 500 ppmV/compound) for the dilution bottle mixture.

The sample format consisted of Pyrex tubes (10 cm long, 1.5 cm o.d., and 1.2 cm i.d.) packed with 1.35 g of TENAX-GC and capped at both ends with glass wool. These cartridges were initially baked out at 270°C to remove any residual contamination and then attached to a zero grade helium purge system. Known volumes of the gas mixture (typically 50 to 100 µL) were injected into this purge system, which served to deposit the analytes onto the TENAX-GC. After being loaded, the sample cartridges were individually sealed in glass vials with Teflon-lined caps. A typical sample set of five to ten vials was placed in a container partially filled with activated charcoal and then stored in a freezer at the NSI facility until needed.

INSTRUMENTATION

The analytical instrumentation incorporates three subsystems, each of which is commercially available. They are: 1) a Nutech model 320 cartridge desorption and sample injection system (Nutech Corp., Durham, NC); 2) a Varian 3700 gas chromatograph (Varian Associates Inc., Palo Alto, CA); and 3) an IBM model 9195 Fourier transform infrared spectrometer (IBM Instruments, Inc., Danbury, CT). These have been interfaced for split-less on-column injection and subsequent serial infrared and flame ionization detection (FID), using the IBM Model F2752 on-the-fly (light pipe) GC/FTIR interface attachment and the GC's FID. A block diagram of the overall system is given in Figure 1.

At the start of a GC/FTIR run, a loaded Tenax-GC cartridge is placed in the thermal desorption chamber. The carrier gas flows through the desorption chamber, and entrains sample desorbed from the cartridge. Since Tenax, like other solid sorbents, has many of the properties of a chromatographic stationary phase some compounds will be preferentially retained on the sorbent, and the rates of thermal desorption will vary from compound to compound.

To assure that all components of the gas mixtures enter the GC at the same time, compounds are cryogenically trapped at -150°C until the desorption procedure has been completed (typically about 30 minutes). At the end of this time, the trap is quickly heated to 200°C, and the sample is flashed onto the GC capillary column, where it is cryofocused at the head of the column at -50°C.

As compounds elute from the GC column during programmed heating to 150°C, they pass into the FTIR light pipe, which is the heart of the GC interface. IR light from the FTIR source is focused through the 1 mm gold coated bore of the 35 cm long pyrex tube (light pipe) onto a LN_2 cooled MCT detector.[7] As compounds pass through the light pipe, 5-6 interferograms are collected per peak and saved for later computation. Data are collected using the Gram-Schmidt algorithm. This algorithm involves the computation of a single point interferogram based on the average of the total absorption detected by each scan relative to the signal from the carrier gas. These single points constitute a real-time chromatogram, referred to here as the Gram-Schmidt (G-S) trace. After passing through the light pipe for IR detection, the eluant reenters the GC, and is monitored by the standard flame ionization detector. The signal from the FID follows the FTIR (G-S) peak by ca. 3 sec.

After the GC run is completed, the interferograms corresponding to each of the eluant peaks are co-added, and the FTIR spectra of each compound is generated. The resulting FTIR spectra can then be compared to the Sadtler IRVAP 8x16 library of 8000 vapor phase spectra of organic compounds, which is stored on disk. The library search program returns the 10 best spectral matches and an associated "Hit Quality" number for each in the range 0 to 1000 (1000 indicates a perfect match).

One of the characteristics of the combination of these three techniques, TENAX thermal desorption, GC and FTIR, is the inevitability of the presence of background water in the system. Under normal GC operation, the presence of small amounts of water vapor in the column is unimportant because the FID is relatively insensitive to it. However, because of the sensitivity of IR to water, it is necessary to reduce the level of water in the GC/FTIR system. For this purpose a Perma-Pure dryer has been inserted between the desorption chamber and the trap. The Perma-Pure dryer consists of two concentric tubes, the inner one, which carries the GC effluent, made of Nafion, and the outer, of Teflon. Polar compounds such as water readily permeate the Nafion and are purged by a flow of dry nitrogen in the annular space between the tubes.

RESULTS

In order to evaluate the combined systems, preliminary separation and spectral determinations were made using relatively concentrated gas mixtures injected directly into the helium purge line of the Nutech desorption unit. Two analysis runs were made on replicate samples, first without the Perma-Pure dryer and then after insertion of the dryer. The FTIR Gram-Schmidt trace shows dramatically the interference of H_2O with the IR detection. Without the dryer (Figure 2), the broad double maximum band from the H_2O extends from 13-18 minutes and virtually masks peak 9. After insertion of the dryer (Figure 3), the water band extends only from 13 to 15 minutes. The presence of water vapor at these target compound levels does not appear serious, even in the sample run without the dryer. However, at the few hundreds of nanograms level, as shown below, the removal of as much water as possible is imperative. Even at this higher loading level the importance of the reduction in water can be demonstrated by looking at some of the less intense G-S speaks. Peak 9 (Figures 2 and 3), for example, is barely visible in the trace run without the dryer since it is nearly lost under the background water band. However, this peak is clearly revealed when the dryer is employed.

The transform of the co-added interferograms collected during the interval of peak 9 is presented in Figures 4 and 5. The spectrum in Figure 4 was obtained without the Perma-Pure dryer, and it is evident that much of the spectrum is obscured by the adsorption of water. When the dryer is employed, all of the background water disappears, and the spectrum of peak 9 is revealed, as seen in Figure 5. When the spectrum taken without the dryer was subjected to the vapor phase library search, it was found that the automatic peak picking routine ignored some of the peaks which were due to the sample, and chose a peak due to the water absorption; this resulted in a mis-identification of the spectrum. However, when the water was eliminated, the routine properly chose peaks only due to the sample. The spectrum of peak 9 was correctly identified as trichloroethylene.

The G-S trace of a mixture of several sets of isomeric compounds loaded onto Tenax at about 380-580ng levels is shown in Figure 6. The G-S trace shows the greater importance of the background water band for samples loaded at these levels. The actual chromatographic peaks are barely visible, but still are clearly above the baseline. Note that all of these compounds elute after the broad water "band". An expanded view of the 18-24 minute portion of the G-S trace is shown in Figure 6b. Eight compounds were loaded on the cartridge, and seven peaks were distinctly observed (in agreement with the post-light pipe FID chromatogram). The interferograms corresponding to each of the seven peaks were co-added and transformed and then were corrected by subtracting a background generated from interferograms collected adjacent to each peak. For example, the results of co-added interferograms collected during the passage of peak 6

(Figure 6) through the light pipe is shown in Figure 7. This figure shows: a) the spectrum of the adjacent background, b) the uncorrected spectrum and, c) the background corrected spectrum. The spectral search results using the Sadtler IRVAP 8X16 library and associated search program are given in Table I for peak 6. (It should be noted that the automatic scale expansion feature of the plotting program gives different absorbance scales for parts (a), (b) and (c) of Figure 7. The intensity of the background correction was adjusted so as to give a flat baseline with no negative excursions). This procedure was repeated for all of the remaining peaks (Figure 6). The subtracted spectra were then submitted to the library search program for identification. The results of the library searches are tabulated in Table II for all the peaks. In only one case did the search fail to select the known compound in the ten best hits. From independent evidence (supplied by NSI) peak 1 is known to contain both m-, and p-xylene with essentially no resolution between the two compounds. Since the bands of both isomers are present in the spectrum, the search (which presumes the spectrum is of a single compound) could not make a correct identification. Ortho-xylene, which elutes separately, is identified from the corrected spectrum from peak 2 as hit 10 by the spectral search routine.

Of the other isomer sets in the mixture, all are clearly identified. Particularly impressive is the generation of the separate isomer spectra of o-, m-, and p-chlorotoluenes, despite the overlap of their peaks in both the FID and FTIR chromatograms (peaks 3-5, Figure 6). The spectra were obtained by co-adding interferograms from each of the components separately (#'s 3, 4, and 5). The ortho- isomer is hit 7, the meta-, hit 1, and the para-, hit 2 when the background corrected spectra of peaks 3, 4 and 5 are subjected to the standard search routine. Meta- and ortho-dichlorobenzene are both identified as hit 1 when the library is searched for the background corrected spectra prior to running the spectral search routine. The transform of the coadded interferograms of peak 1 of the isomer mixture was known to be either m-xylene, p-xylene, or a mixture of both (see Figure 8). Because the library failed to identify it as either of the two independent isomers, and because it is well-known that these isomers coelute, peak 1 was assumed to be the combination of these two compounds. In order to test this hypothesis a user-generated library spectrum of m-xylene was subtracted from the presumed combination spectrum. The resulting spectrum shown in Figure 9 as then submitted to the library search program. The library search successfully identified the resulting spectrum as that of p-xylene, confirming the hypothesis.

CONCLUSIONS

The results illustrate that thermal desorption GC/FTIR, using commercially available equipment and TENAX-GC cartridges, is capable of distinguishing geometric isomers of compounds with moderately intense IR bands at loadings of 300-500 ng per compound per cartridge. Unequivocal, general identification in conjunction with GC retention time data would be aided by the availability of a user generated library of target compounds. Traces of water desorbed from the cartridges create a problem with the method but can be reduced to manageable levels by insertion of a drying element. With improvements in the method of detecting peaks in the Gram-Schmidt trace it is likely that the detection/identification limit for the method could be ca. 100 ng per compound per cartridge.

REFERENCES

(1) Shafer, K.H.; Lucas, S.V.; Jakobsen, R.J. *J. Chromatog. Sci*. 1979, 7, 464-470.

(2) Gurka, D.F.; Betowski, L.D. *Anal. Chem*. 1982, 54, 1819-1824.

(3) Shafer, K.H.; Hayes, T.L.; Brasch, J.W.; Jakobsen, R.J. *Anal. Chem.* 1984, 56, 237-240.

(4) Gurka, D.F.; Umana, M.; Pellizzari, E.D.; Moseley, A.; deHaseth, J.A. *Appl. Spectrosc*. 1985, 39, 297-303.

(5) Pellizzari, E.D.; Carpenter, B.H.; Bunch, J.E.; Sawicki, E. *Environ*. *Sci*. *Technol*. 1975, 9, 556-560.

(6) Pellizzari, E.; Demian, B.; and Krost, K. *Anal*. *Chem*. 1984, 56, 793-798.

(7) Garlock, S.E.; Adams, G. E.; Smith, S. L *Am. Lab*. 1982, 14 (Dec), 48-55.

TABLE I

SADTLER IR-VAP 8X16 LIBRARY SEARCH REPORT FOR PEAK 6 IN GC-FTIR OF ISOMER MIXTURE (M-DICHLOROBENZENE)

HIT NO.	HIT QUALITY	SPECTRUM NO.	COMPOUND NAME
1	294	1597	BENZENE, M-DICHLORO-
2	286	7524	BENZENESULFONICACID,1-METHYL-1,2,3,3-TETRAFLUOROPROPYLESTER
3	266	535	PYRIDINE,2-CHLORO-
4	254	5856	ETHER,BIS/2-/2,4,5-TRICHLOROPHENOXY/ETHYL/
5	210	6989	ETHANOL,2-/2-/2-CHLOROETHOXY/-ETHOXY/-
6	206	5600	ACETALDEHYDE,2-PHENOXY-, DIETHYL-ACETAL
7	142	3406	ACETONITRILE,METHOXY-
8	102	4579	METHANE,BROMOTRIFLUORO-
9	86	5626	THIOCYANICACID,4-HYDROXY-2,3-XYLYLESTER
10	78	3023	S-TRIAZINE,2,4,6-TRIS/ALLYLOXY/-

Hit No. indicates the rank of best 10 matches from the 8000 library spectra.

Hit Quality indicates "goodness of fit" of subject spectrum to the indicated library spectrum, range 0 to 1000.

TABLE II

RESULTS OF SADTLER LIBRARY SEARCH FOR GC-FTIR SPECTRA FROM ISOMER MIXTURE

PEAK NO.	COMPOUND*	HIT NUMBER	HIT QUALITY
1	M,P-XYLENE	-	-
2	O-XYLENE	10	262/434
3	O-CHLOROTOLUENE	7	380/500
4	M-CHLOROTOLUENE	1	444/444
5	P-CHLOROTOLUENE	2	658/676
6	M-DICHLOROBENZENE	1	294/294
7	O-DICHLOROBENZENE	1	310/310

*FROM INDEPENDENT IDENTIFICATION

Hit number indicates the rank of the match of the subject spectrum to the correct library spectrum.

Hit Quality is expressed as a ratio where the first number indicates "goodness of fit" of the subject spectrum to the correct library spectrum, and the second number indicates "goodness of fit" of the subject spectrum to the #1 ranked (but possibly incorrect) match.

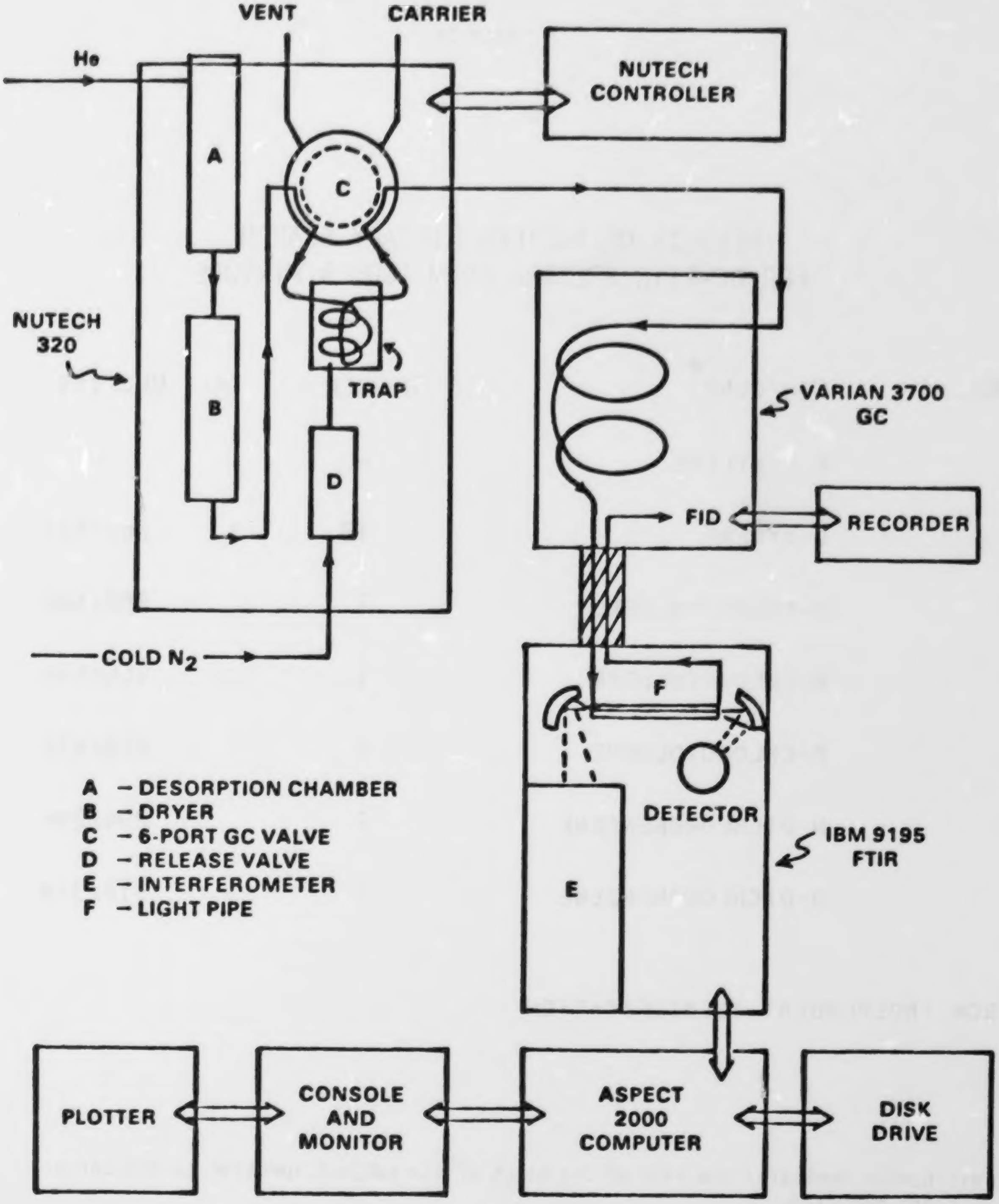

VENT
CARRIER
He
NUTECH CONTROLLER
A
C
NUTECH 320
B
TRAP
D
VARIAN 3700 GC
FID
RECORDER
COLD N2
F
A – DESORPTION CHAMBER
B – DRYER
C – 6-PORT GC VALVE
D – RELEASE VALVE
E – INTERFEROMETER
F – LIGHT PIPE
DETECTOR
IBM 9195 FTIR
E
PLOTTER
CONSOLE AND MONITOR
ASPECT 2000 COMPUTER
DISK DRIVE

Figure 1. Block diagram of thermal desorption-GC/FTIR system.

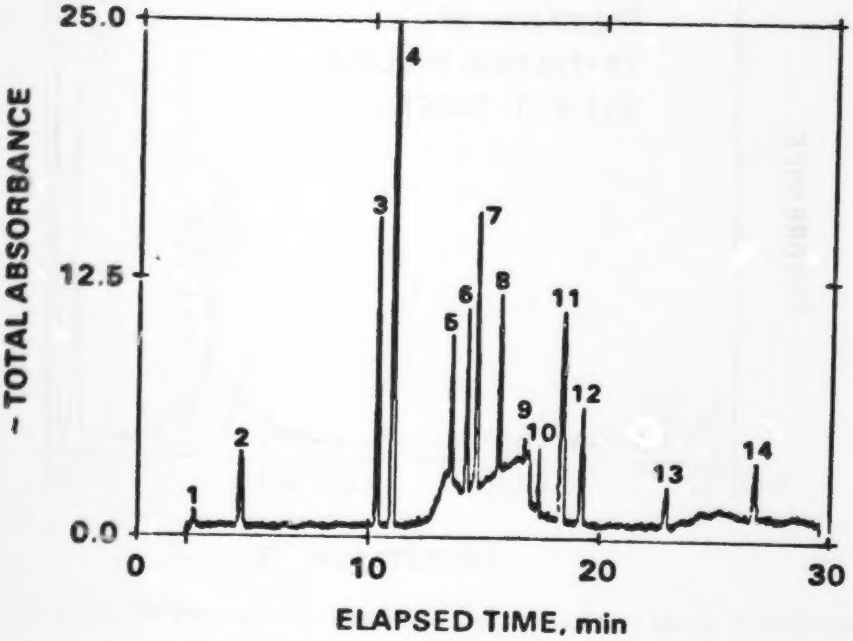


Figure 2. GC/FTIR Gram-Schmidt trace of initial test sample mixture containing 14 halo-organic compounds obtained without use of Perma-Pure dryer.

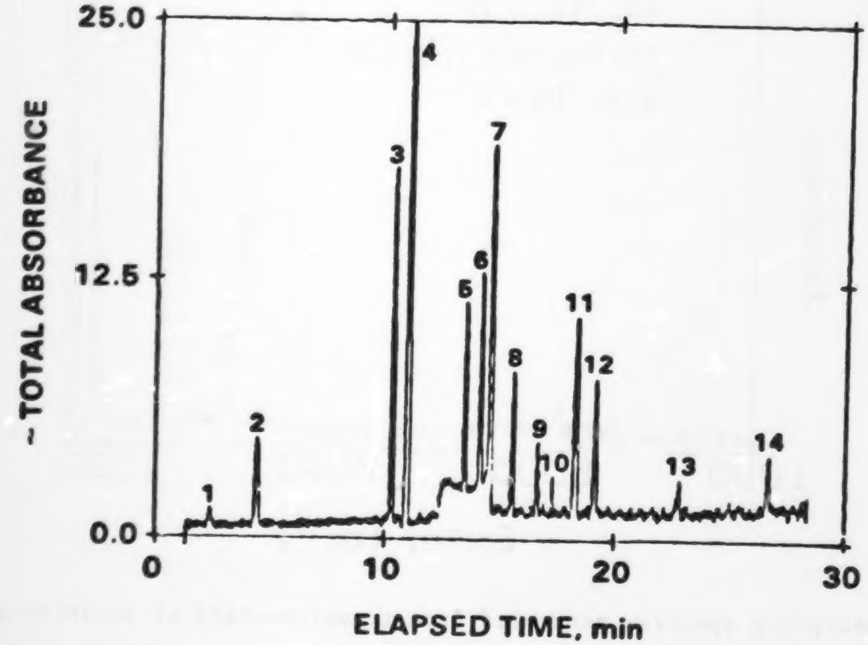


Figure 3. CG/FTIR Gram-Schmidt trace of initial test sample mixture containing 14 halo-organic compounds obtained with use of perma-Pure dryer.

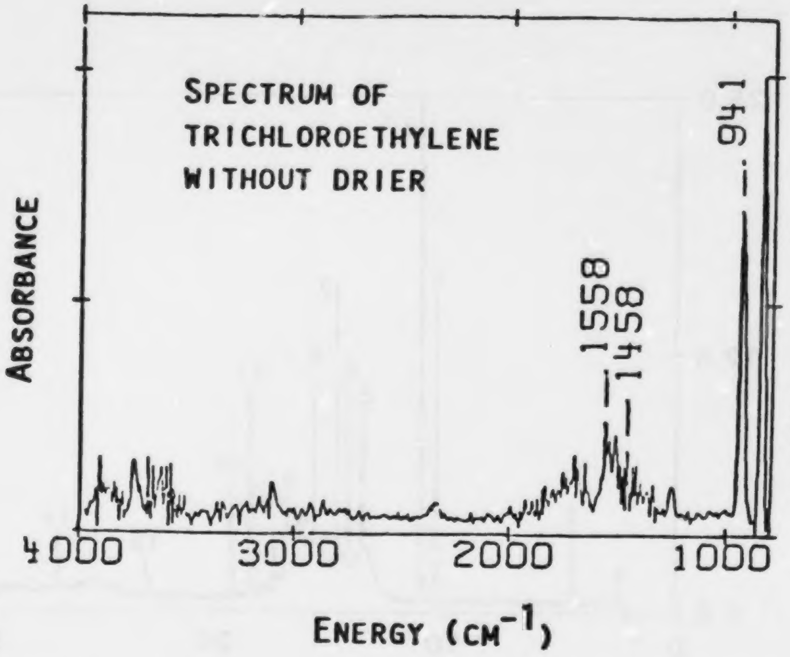


Figure 4. Absorption spectrum generated from transformation of interferograms collected during passage through the light pipe of peak 9 in Figure 2 (without dryer).

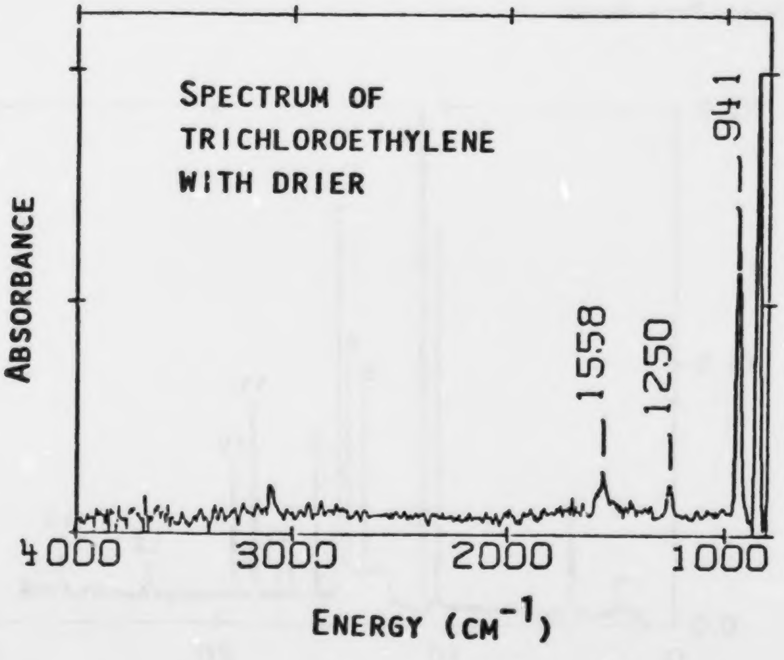
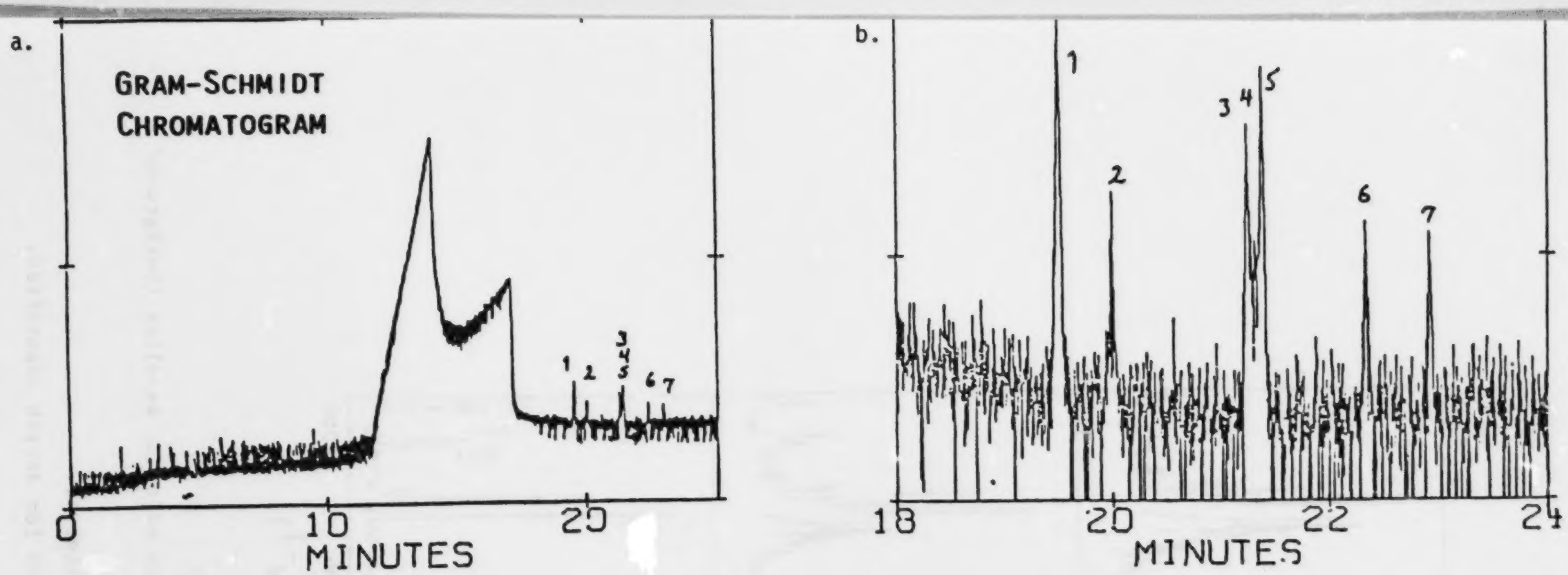


Figure 5. Absorption spectrum generated from transformation of interferograms collected during passage through the light pipe of peak 9 in Figure 3 (with dryer). Identified as trichloroethylene by library search.



PEAK NO.	COMPOUND	CONCENTRATION
1	M,P-XYLENE	381, 389 NG
2	O-XYLENE	380 NG
3	O-CHLOROTOLUENE	477 NG
4	M-CHLOROTOLUENE	473 NG
5	P-CHLOROTOLUENE	471 NG
6	M-DICHLOROBENZENE	567 NG
7	O-DICHLOROBENZENE	575 NG

Figure 6. GC/FTIR Gram-Schmidt trace for analysis of mixture of sets of isomeric compounds listed.

a) Full 25-minute Gram-Schmidt trace

b) Expansion of the 18-24-minute region of the G-S trace during which time all of the compounds elute.

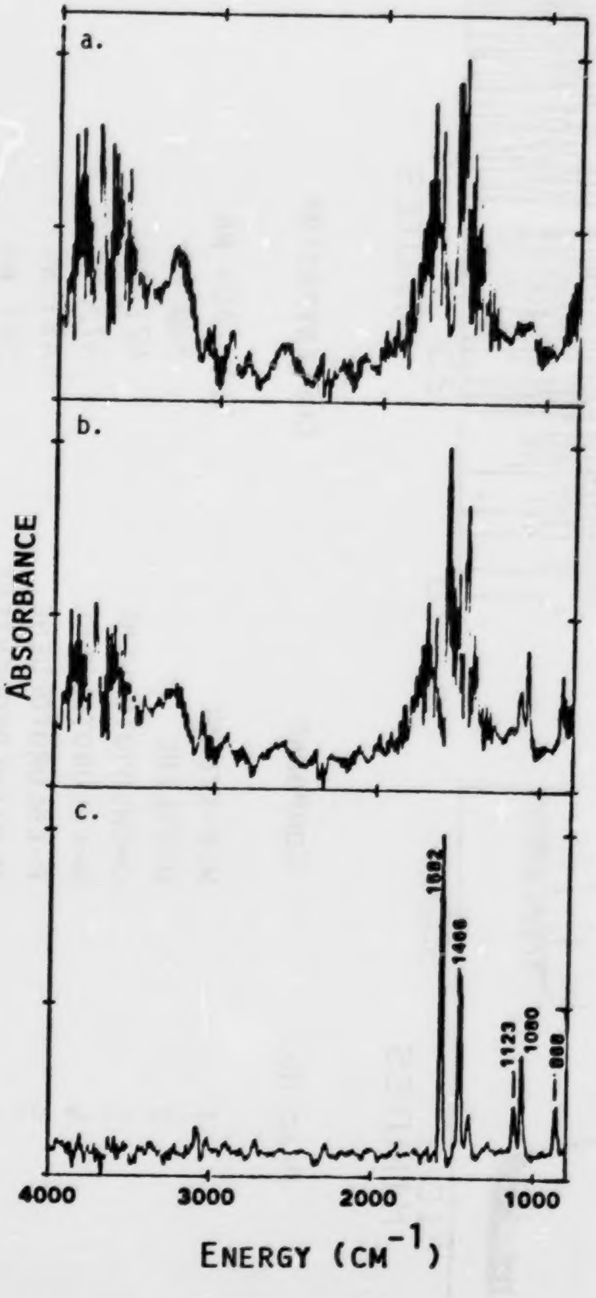


Figure 7. Peak 6, Figure 6 (m-dichlorobenzene)

a) Absorption spectrum generated from adjacent baseline (background correction).

b) Uncorrected spectrum from peak interval.

c) Corrected spectrum with peaks used for search identified.

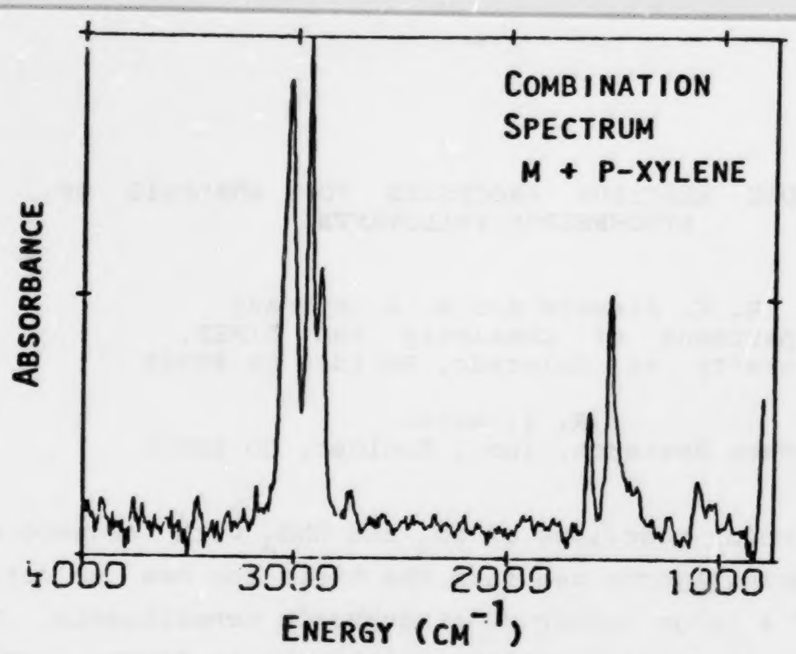


Figure 8. Background corrected absorption spectrum generated from peak 1, Figure 6. Combination spectrum at m, p-xylene.

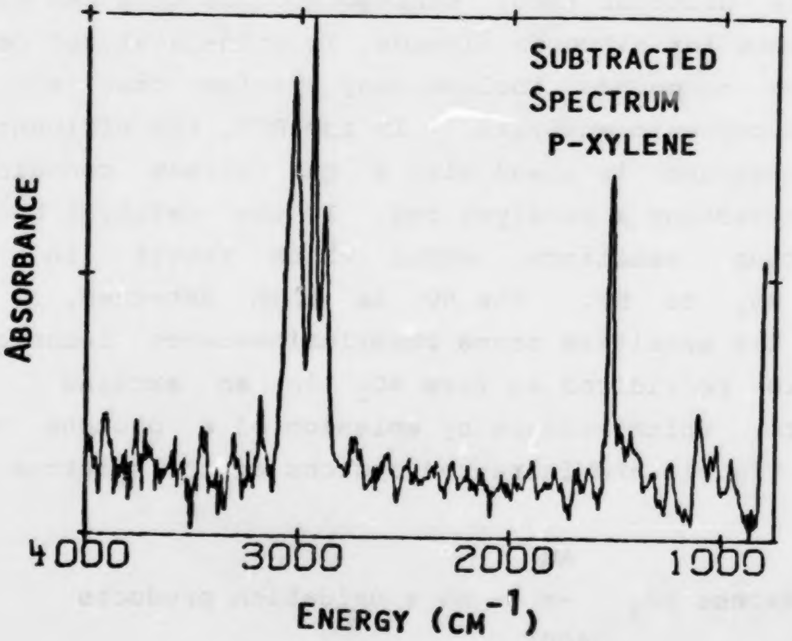


Figure 9. Spectrum of p-xylene generated from the subtraction of a library spectrum of m-xylene from the combination spectrum in Figure 8.

NEW REDOX REACTION PROCESSES FOR ANALYSIS OF ATMOSPHERIC POLLUTANTS

R. E. Sievers and S. A. Nyarady
Department of Chemistry and CIRES,
University of Colorado, Boulder CO 80309

R. S. Hutte
Sievers Research, Inc., Boulder, CO 80301

Catalyzed redox reactions of NO_2 and HNO_3 with organic and inorganic reducing agents can form the basis for new selective measurements of a large number of atmospheric constituents. The unifying feature of these reactions is that NO is formed, which can be selectively and sensitively detected downstream by the well-established ozone chemiluminescence technique (Fontijn, A., et al, 1970).

A new selective detector for gas chromatography has recently been developed (Nyarady, S. A., et al., 1985). The redox chemiluminescence detector (RCD) sense compounds that can serve as reducing agents for nitrogen dioxide, in gold-catalyzed redox reactions. These compounds include many species that are of importance in atmospheric analyses. In the RCD, the effluent of the gas chromatograph is mixed with a gas stream containing NO_2 prior to contacting a catalyst bed. In the catalyst bed, oxidation/reduction reactions occur which result in the conversion of NO_2 to NO. The NO is then detected, downstream, by the sensitive ozone chemiluminescence technique, in which NO is reoxidized to form NO_2 in an excited electronic state, which relaxes by emission of a photons with energies in the visible and infra-red regions of the spectrum.

$$\text{Formaldehyde} + \text{excess } NO_2 \xrightarrow[400^{\circ}\,C]{Au} NO + \text{oxidation products}$$

$$NO + O_3 \rightarrow NO_2 + O_2 + h\nu$$

Compounds that can act as reducing agents for NO_2 in these catalyzed redox reactions include formaldehyde and other aldehydes, phenols, alcohols, ketones, esters, ethers, carboxylic acids, aliphatic and aromatic amines, olefins, aromatic hydrocarbons, sulfur- and phosphorus-containing compounds, and inorganic species including hydrogen, hydrogen peroxide, ammonia, hydrogen sulfide, sulfur dioxide, carbon monoxide, and phosgene. The sensitivity of the RCD for compounds that can be catalytically oxidized by NO_2 is comparable to the flame ionization detector. Species which do not act as reducing agents in the gold-catalyzed redox reactions with NO_2, and are therefore not detected by the RCD, include the major constituents of air (N_2, O_2, CO_2, Ar), water, and alkanes.

The measurement of organic compounds in ambient air presents many problems to the analytical chemist. Generally, the concentrations of these compounds are very low (ppb-ppt) and therefore require pre-concentration techniques to isolate sufficient quantities of the compounds for the analysis. The samples collected by these techniques, however, are extremely complex. Often the compounds of interest, which are present at very low levels, cannot be directly detected due to the presence of other species, such as aliphatic hydrocarbons, which are present at much higher concentrations. To overcome the complexity of the samples, two techniques are usually employed: fractionation of the sample by chemical and physical techniques,prior to the analysis by a chromatographic method, and selective detectors for gas and liquid chromatography.

Sample fractionation techniques can often be utilized to isolate the compounds of interest from a complex sample matrix. There are, however, many problems associated with these fractionation techniques, including loss of the analytes, contamination of the sample, and incomplete resolution of the compounds of interest from the sample matrix. These techniques are also time-consuming, labor-intensive, and sometimes irreproducible. Another approach is the use of selective chromatographic detectors. By choosing a detector which responds to the compounds of interest, but not to the major components of the sample matrix, analysis of low level species in complex matricies often becomes possible. Selective detectors for gas chromatography commonly used include the electron capture detector for halogenated species, the flame photometric detector for sulfur- and phosphorus-containing compounds, the thermionic flame detector for nitrogen compounds and the photoionization detector for aromatic hydrocarbons. Until now, there has been no detector that exhibits selectivity for oxygen-containing compounds.

It is for these reasons that the development of a new selective detector will enhance our capabilities to handle more effectively the complex mixtures often encountered in environmental analysis. The selectivity of the RCD can be varied by changing the operating parameters such as the temperature of the catalyst chamber, the active metal used as the catalyst, and the reagent gas (NO_2 versus HNO_3). For example, at low catalyst temperature (<200°C), only those compounds which are most easily oxidized produce a RCD response, while at higher temperature, a greater number of compounds can serve as reducing agents for NO_2, and, therefore, are detected.

Because the RCD does not respond to the major constituents of air or to saturated hydrocarbons, it is ideally suited for the analysis of low levels of oxygen-, nitrogen-, sulfur-, and phosphorus-containing compounds in ambient air and associated with airborne particulate matter. The RCD can also detect some gases which cannot be sensitively detected by other GC detectors. Potential applications of the RCD in atmospheric analysis include the measurement of aldehydes and other oxygenates(in the presence of much higher levels of hydrocarbons), measurement of H_2O_2 in air and precipitation, the analysis of ammonia and amines in air, and the selective measurements of olefins and aromatic compounds in urban air. Specific hazardous air pollutants to which the RCD has been shown to be sensitive include acetaldehyde, formaldehyde, benzene, toluene, phenol, o,m,p-cresol, acrolein, 1,3-butadiene, ethylene oxide, vinyl chloride and phosgene.

When pre-concentration techniques such as cryogenic sampling or collection on porous polymers are used for the analysis of volatile organic compounds in urban air, the major components are aliphatic and aromatic hydrocarbons, primarily from the incomplete combustion of fossil fuels. Because these compounds are present at fairly high levels, and so numerous, they overlap with and prevent detection of minor species such as aldehydes and other oxygenates. The RCD permits the detection of these oxygenates without interferences from the ubiquitous aliphatic hydrocarbons.

In the analysis of organic compounds associated with airborne particulate matter, the RCD should permit detection of the polycyclic aromatic hydrocarbons, and the nitro-, amino-, and oxygenated- derivatives of the PAH's without the use of pre-fractionation techniques, even if higher concentrations of aliphatic hydrocarbons are also present.

The principle of catalyzed redox reaction can also be used to detect odd nitrogen species in ambient air (Bollinger, M. J., et al.,). Hubler, et al., have described the continuous measurement of the sum of total reactive odd nitrogen compounds in ambient atmosphere.

Nitric acid, nitrogen dioxide, PAN and other unidentified nitrogen-containing species in rural tropospheric air were converted continuously to nitric oxide by addition of excess carbon monoxide on a catalytic gold surface. By judicious choice of the reducing agent, selective detectors for such species as HNO_3, PAN, and organic nitrates may be possible. Alternatively, selective pre-concentration sorption techniques used in concert with catalysis of redox reactions may allow measurement of species such as nitric acid at lower levels than presently possible. For example, we have demonstrated that nitric acid becomes adsorbed on gold surfaces, where it becomes activated and rapidly reacts with alcohols to form NO. This may allow pre-concentration of one or more odd nitrogen species from ambient air on gold sorbent surfaces, followed by intermittent injection of an excess of a reducing agent such as ethanol, coupled with rapid heating to generate a pulse of nitric oxide which can be measured by chemiluminescence as a peak downstream according to the following reaction sequence:

$$\mathrm{Au{:}HNO_3 + excess\ C_2H_5OH} \rightarrow \mathrm{NO + oxidized\ products + Au}$$

$$\mathrm{NO + O_3} \rightarrow \mathrm{NO_2 + O_2} + h\nu$$

REFERENCES

1. Bollinger, M. J., Sievers, R. E., Fahey, D. W., Fehsenfeld, F. C., Anal. Chem. 55,1980-1986, 1983.

2. Fontijn, A., Sabadell, A. J., Ronco, R. J., Anal. Chem. 42, 575, 1970.

3. Hubler, G., Fahey, D. W., Williams, E. J., Eubank, C. S., Murphy, P. C., Norton, R. B., Parish, D. D., Fehsenfeld F. C., Albritton, D. L., American Geophysical Union Meeting, San Francisco, CA, Dec. 1984.

4. Nyarady, S. A. Sievers, R. E., J. Amer. Chem. Soc.,107, in press 1985; Nyarady, S. A., Barkley, R. M., and Sievers, R. E. Anal. Chem. 57, in press, 1985.

APPLICATION OF MULTIDIMENSIONAL GAS CHROMATOGRAPHY TO THE ANALYSIS OF PARTICULATE SAMPLES

Stanley L. Kopczynski
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

INTRODUCTION

A Sichromat-2 Gas Chromatography System was employed to evaluate the applicability of multidimensional gas chromatography (MDGC) to the analysis for polycyclic aromatic hydrocarbons (PAHs) extracted from particulate samples. The possibility of shortening the analysis time by using unfractionated sample extracts with MDGC was also investigated.

MDGC systems typically consist of two chromatography columns connected in tandem and composed of stationary phases of different polarities and/or operated at different temperatures or with different temperature programs. Sample preparation for single column gas chromatography (GC) generally requires lengthy and laborious extraction and fractionation procedures to avoid uncertainties in analyte identification and quantitation. The heart-cutting technique used in two-stage chromatography produces superior separations compared to a single column of comparable length. It is a means by which analytes in complex mixtures may be isolated without prior sample fractionation. MDGC has been used successfully with a variety of complex mixtures including food, crude oil fractions, and water(1,2,3).

EXPERIMENTAL

The Siemens Sichromat-2 chromatograph used in this study contained two fused silica open tubular (fsot) columns coupled in series through a T-piece which is designed to switch eluates pneumatically from the first stage column (polar) to the second stage column (nonpolar) without valves and without a sample trap (Figure 1). Connection between the two columns is made by means of a loosely fitting capillary contained in the T-piece. The auxiliary gas pressure at each end of the capillary is adjusted by means of needle valves NV2 and NV3. Column 1 effluent, which is normally directed to the column 1 detector, can be switched to column 2 by activating the (bypass) solenoid valve, MV2. The two columns are contained in separate ovens operated with separate temperature controls, allowing analytes cut from the first column to be focused at a reduced temperature on the second column. Non-vaporizing on-column injections were made by means of a Varian on-column capillary injector.

The column of choice for the first stage was DB-210, 15 m x 0.32 mm (J & W Scientific, Inc.). Tests with more polar columns showed excessive column bleed and excessive tailing of the solvent and the higher molecular weight PAHs. A DB-5 column, 20 m x 0.32 mm, (J & W Scientific, Inc.) was employed in the second stage.

An 8.3 eV HNU photoionization detector was employed together with a flame ionization detector for the back (second stage) column to provide increased confidence in the identification of PAHs.

The evaluation was conducted with selected PAHs occurring in atmospheric aerosols. Test mixtures consisted of the National Bureau of Standards (NBS) Standard Reference Material (SRM) 1647 and standards prepared on-site by Northrop Services, Inc. The toluene solvent employed was chromatography grade from Burdick and Jackson. The NBS urban dust sample SRM 1649 served as a test atmospheric particulate sample. In the absence of electronic integration, analyses were based on peak height measurements.

The extraction procedure for SRM 1649 consisted of two successive extractions of a 1 g sample with 5 mL toluene in an ultrasonic bath for 45 min at 60°C. Each extract was centrifuged and decanted yielding a black mixture. They were filtered twice with a Waters Associates' sample clarification kit, yielding a deep yellowish-brown solution. The filtered extract was concentrated in a test tube to 0.5 mL by directing a gentle flow of nitrogen gas onto the surface of the solution.

RESULTS AND DISCUSSION

A comparison of splitless and on-column injections showed that large on-column injections (5μL) could be made without sacrificing chromatographic resolution. However, this did produce a higher solvent background, which resulted in an increased limit of detection (LOD) with the front column. Back column LOD for PAHs was generally 0.2-0.3 ng while the front column LOD was 5-70 times higher.

Results with SRM 1649 indicate that with an atmospheric particulate concentration of 100 $\mu g/m^3$ a high volume sampler will collect more than enough particulate matter for quantitative FID measurements on the back column. However, the amount collected will be generally inadequate for PID measurements or FID measurements of front column effluents. The high limit of detection observed with the PID may be inherent in the lamp or may be due at least in part to aging of the lamp during the course of the study.

The concentrated toluene extract of SRM 1649 produced a strong unresolved envelope of response on the front column and completely obscured the presence of trace quantities of PAHs, as shown in chromatogram A of Figure 2. Heart-cuts for particular PAHs were taken at time intervals determined from calibration runs. The PAHs were identified by elution times in the FID chromatogram of the back column. Confirmatory identification by the PID was not possible due to the low and unstable response of the 8.3 eV lamp. As illustrated in the case of pyrene (chromatogram B, Figure 2) heart-cuts from the raw extract contain many components in addition to the PAH. Consequently very accurate and reproducible elution time measurements as well as high resolution in the back column are required for identification and measurement of the analyte of interest. Mean elution times, mean peak heights, and standard deviations obtained for 2 μL on-column injections of several PAHs are presented in Table 1. Elution times are very reproducible, especially on the second-stage column.

Low recoveries were obtained for the 5 PAHs found in SRM 1649 (Table 2). Benzo(b)fluoranthene and benzo(k)fluoranthene were not found although the NBS reports them to be present at concentrations comparable to pyrene and B(a)P. No additional fluoranthene or pyrene could be found in a re-extraction of SRM 1649, suggesting the possibility of volatilization losses of these two compounds while concentrating the extract.

Grosjean(4) has reported incomplete extraction of ambient particulate matter by ultrasonication with toluene. This possibility is supported by the 85% recovery of B(e)P achieved in very recent extractions in our laboratory using a Sonifier Cell Disruptor (Heat Systems-Ultrasonics, Inc.) and methylene chloride in place of toluene. However column degradation cannot be ruled out as a contributor to losses of the less volatile PAHs. Column degradation was very evident in subsequent analyses of standard mixtures and was found to be irreversible.

CONCLUSIONS

Multidimensional GC has been found to be capable of analyzing complex atmospheric mixtures for PAHs. Limited success was achieved in developing a fast and simple analysis for PAHs in atmospheric particulate samples. Some sample clean-up prior to analysis is required to protect the GC system from "bad actors" present in the unfractionated extract. Extraction of atmospheric particulate matter with toluene in an ultrasonic bath yields insufficient recovery of PAHs.

The multidimensional gas chromatograph system used in this study performed reliably and reproducibly with both splitless and on-column sample injections. Although larger sample sizes can be employed with on-column injections, the full potential of this technique was not realized in this study due to the limited capacity of the front capillary column.

Multiple detectors are highly desirable for analysis of complex mixtures containing analytes at trace concentrations. However, the 8.3 eV PID is not recommended as an auxiliary detector for PAHs because of its short life and low sensitivity. Better results can be expected with a lamp of greater intensity such as the 9.5 eV PID or a mass selective detector.

REFERENCES

1. H. J. Stan and D. Mrowetz, "Residue Analysis of Organophosphorus Pesticides in Food with Two-Dimensional Gas Chromatography Using Capillary Columns and Flame Photometric Detection", J. of High Resolution Chromatography and Chromatography Communications, 6:255-263 (1983).

2. Anders Jonsson and Sven Berg, "Determination of Low-Molecular Weight Oxygenated Hydrocarbons in Ambient Air by Cryogradient Sampling and Two Dimensional Gas Chromatography", J. of Chromatography, 279:307-322 (1983).

3. Gerhard Schomburg, "Multidimensional Gas Chromatography as Sampling Techniques", in "Sample Introductin in Capillary Gas Chromatography"; Peter Sandra, Ed.; Heutig Publishing, Inc.: Stamford, CT., 1985; PT. 1, pp 235-260.

4. Daniel Grosjean, "Polycyclic Aromatic Hydrocarbons in Los Angeles Air from Samples Collected on Teflon, Glass and Quartz Filters", *Atmos. Envir.*, 17: 2565-2573 (1983).

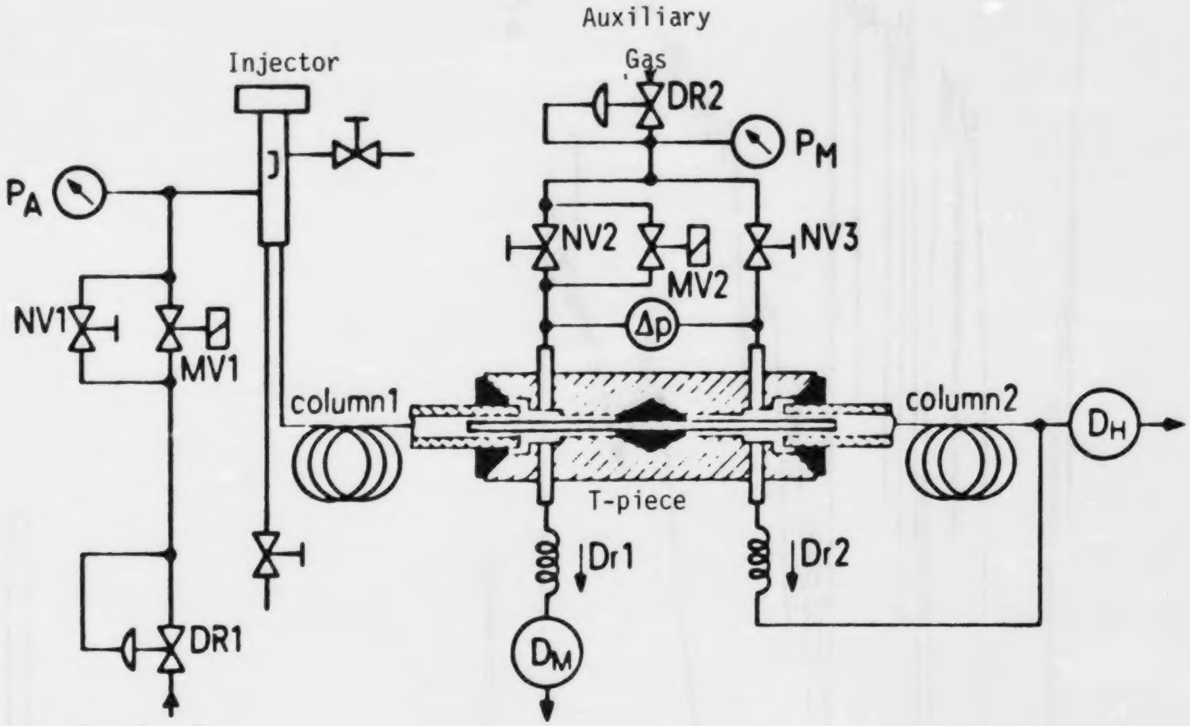

Auxiliary
Gas
DR2
Injector
J
P_M
P_A
NV2
MV2
NV3
NV1
MV1
Δp
column1
column2
D_H
T-piece
Dr1
Dr2
DR1
D_M
Carrier Gas

Figure 1. **COLUMN SWITCHING DEVICE**

P_A, P_M: Pressure Gauges
DR1, DR2: Pressure Regulators
ΔP: Differential Pressure Monitor
NV1, NV2, NV3: Needle values
MV1, MV2: Solenoid Valves
Dr1, Dr2: Capillary Restrictors
D_M: Column 1 Detector
D_H: Column 2 Detector

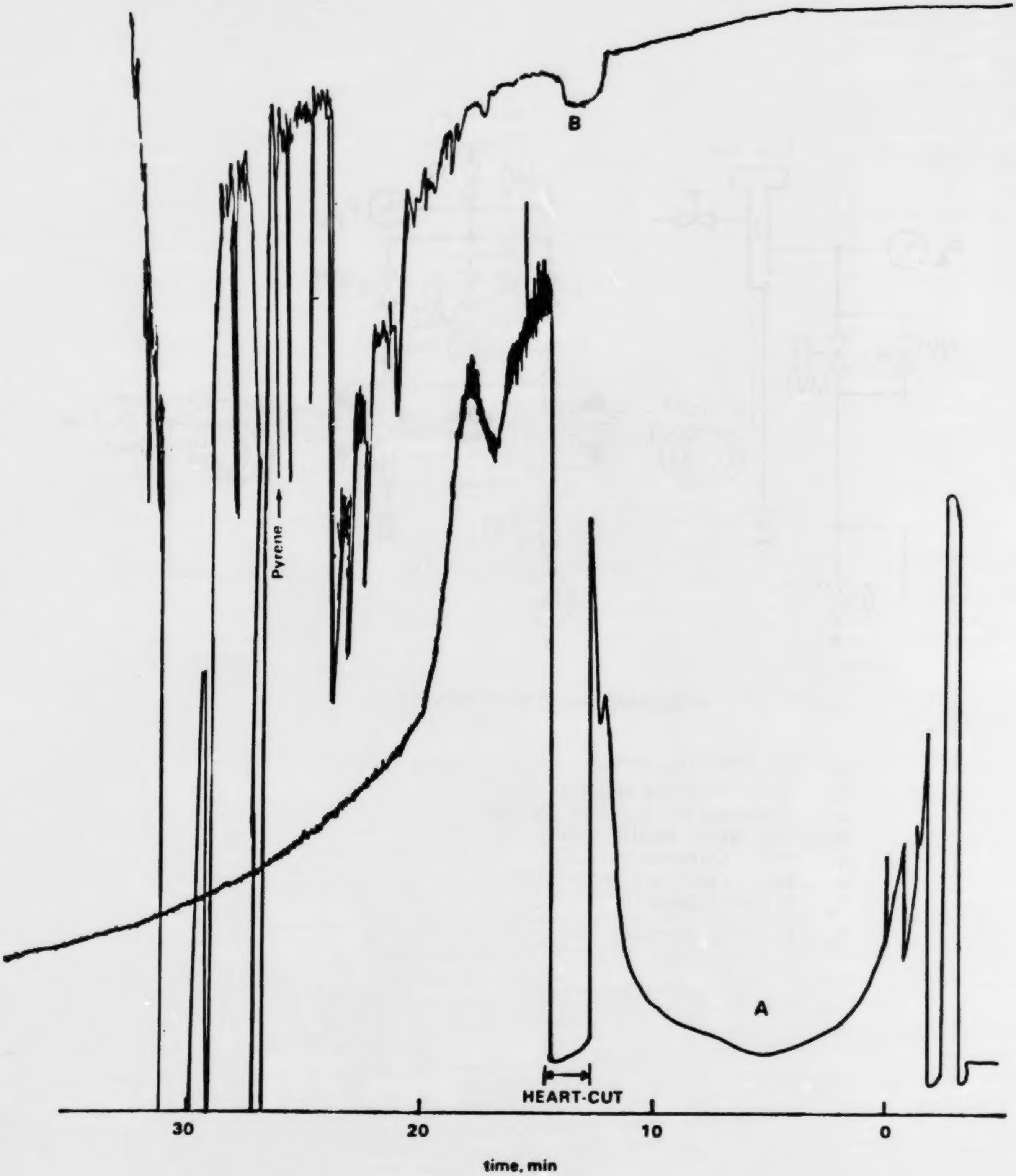


FIGURE 2. 2.0μL raw toluene extract of SRM 1649: Pyrene heart-cut on A, Front column, and B, Back column.

TABLE 1

Analytical Precision of FID Measurements with On-Column Injections of Standard Mixtures of PAH's

	First-Stage Column		Second-Stage Column	
	Mean Elution Time (min)	Mean Peak Height(mm)	Mean Elution Time(mm)	Mean Peak Height(mm)
Pyrene	13.74(0.02)		19.58(0.01)	65.1(5.4)
Chrysene	16.04(0.02)	64.8(2.8)	24.32(0.01)	108.3(4.4)
Benzo(e)pyrene	21.43(0.02)	47.5(2.1)	36.68(0.00)	121.6(2.6)
Benzo(ghi)perylene	33.39(0.01)	36.1(0.6)	47.99(0.01)	103.2(4.9)

TABLE 2

Analysis of SRM 1649 by Chromatographic Heart-cuts of Toluene Extracts

	PAH Concentration in SRM in 1649 (µg/g)			PAH Spike in SRM 1649 Extract (ng)		
	Found	NBS Value	% Recovery	Found	Added	% Recovery
Fluoranthene	3.1	7.1	44			
Pyrene	2.2	6.6	33	10.6	10	106
Chyrsene	2.1	3.6	58			
Benz(a)anthracene	1.3	2.6	50			
Benzo(e)pyrene*	0.64	3.3	19	1.7	10	17

*85% Recovery was achieved in most recent work using a different extraction procedure.

A NEW MICROPROCESSOR-BASED INSTRUMENT FOR THERMAL DESORPTION OF ADSORBENT TRAPS

Robert G. Westendorf
Tekmar Company
P. O. Box 371856
Cincinnati, OH 45222-1856

The analysis of organic compounds in air is performed for a wide variety of reasons, including monitoring of ambient air, emissions studies, and industrial hygiene analysis. The majority of these samples are analyzed by collection on a solid sorbent material, which allows the collection of organics from large volumes of air. The organic compounds are eluted from the sorbent and injected into a gas chromatograph for separation and detection. Elution of the sample from the sorbent is generally accomplished by one of two methods; solvent extraction or thermal desorbtion. Thermal desorbtion generally offers better sensitivity, since the sample is not diluted, better precision, less handling of traps, less cost due to both reusability of traps and elimination of costly high purity solvents, and eliminates the need for hazardous desorbtion solvents. However, thermal desorbtion has not been as popular as solvent extraction for several reasons. The biggest of these has been the lack of availability of a good instrument to perform the thermal desorbtion step. This paper details the design and performance of an innovative new instrument, the TEKMAR Model 5000 Automatic Desorber (Figure 1), that offers high performance, ease of operation, a high degree of flexibility, and operates using the latest in microprocessor technology.

SYSTEM DESCRIPTION

The heart of the new desorber is a tube heater built on a totally new concept. Key features of this new design are ease of sample trap loading and unloading, all flow is positively directed through the trap, traps are loaded when the heater is cool, and it uses a virtually fool-proof, leak-tight sealing method. A representation of the furnace is shown in Figure 2. The trap tube is packed so that approximately 1½" on one end remains empty. An o-ring is placed on the tube, and inserted into the furnace. The cap, which has a second o-ring, is screwed down fingertight, simultaneously compressing both o-rings. The o-ring on the trap tube seals the exterior of the tube, ensuring that all gas used for desorb must flow through the inside of the trap. The second o-ring seals the furnace closure to the outside. Note that both o-rings are located in an area where they are not subjected to heat. In addition, the sample does not come into contact with the o-rings. An injection port into the heater chamber is provided for introduction of standards for calibration or troubleshooting, as well as allowing the Desorber to be used for studies of sorbent capacities. Heaters are rapidly interchangeable (less than 5 minutes) to permit the use of trap tube diameters of 1/4" to 5/8". Each heater can accommodate tubes of two to seven inches.

Loading of the trap into the instrument takes place with the furnace cool. This eliminates the possibility of losing sample compounds before the furnace chamber is sealed. An exclusive Prepurge mode enables gas to be passed through the trap before heating. This mode can serve dual functions: it allows any water present to be purged out of the tube before the internal trap is cooled. This can be particularly helpful for samples taken under high humidity or rainy conditions. The second benefit of prepurge is that it enables oxygen to be completely displaced from the tube before heating. This can dramatically increase the lifetime of the sorbent used, particularly for materials like Tenax, as well as reduce background contamination due to the sorbent.

After prepurge an internal trap is cooled to a preset temperature. This trap can be an open cryogenic trap of narrow or wide bore, or it can be a packed trap with or without cyrogenic cooling. Using liquid nitrogen temperatures down to -150°C can be obtained. The tube heater is then rapidly heated and simultaneously swept with helium to desorb the sorbent. The desorb temperature can be as high as 420°C, allowing the Desorber to be used for carbon-based sorbents such as Spherocarb or Carbotrap. The desorbed materials are then retrapped in the internal trap. After the desorbtion step is complete, an eight port switching valve is rotated to cause the GC carrier gas to backflush the internal trap, which is rapidly heated. The carrier gas is then used to sweep the sample to the GC. For use with capillary columns a second generation cryofocusing trap is used to focus the sample into a very tight band for injection. This cyrofocusing trap can also be operated by itself for the focusing of direct GC injections. The results obtained for a focussed GC injection of an aromatics standard are shown in Figure 3. After the sample is injected, the sorbent trap can be baked to regenerate it. A representation of the gas flow scheme is illustrated in Figure 4.

The control of the instrument is microprocessor-based, and has been engineered to be as user-friendly as possible. The instrument features storage for three methods, one of which enables the operation of the cryofocus interface by itself for focusing direct GC injections of gas standards as specified by EPA methodology (1). All parameters are entered via a tactile response, touchtone membrane keypad. The entire control panel is hinged to allow adjustment to the most convenient angle for parameter entry and to read the two-line LCD display. Building a method can be performed quickly and easily, since all entries are prompted. A powerful GC interface allows the Desorber to fully interact with the chromatograph, permitting the analysis to be fully automated. Additionally, an RS232C data communications port permits the entry or reading of parameters to be performed remotely. A typical use would be allowing the printing of desorbtion parameters on the GC report.

SYSTEM PERFORMANCE

Historically, most thermal desorbtions have been run using an extremely simple chamber. The method of construction of these furnaces allows the flow to pass around the outside of the tube, and not actually pass through it. Desorbtion thus relies on diffusion of the sample compound off the sorbent and out of the tube. This is known as passive desorbtion. The new furnace used in the Model 5000, since it positively directs the gas flow through the trap, provides an active desorbtion. The difference this makes can be seen by comparing the figures listed in Table 1. The conditions under which these figures were obtained, listed in Table 2, are those used by the USEPA for the desorbtion of Tenax tubes used in monitoring of ambient air (1). Recovery values were obtained by the comparison of Tenax cartridges spiked with a gas standard of the indicated compounds versus the same standard directly injected into the GC. By using active desorbtion, the desorbtion efficiencies obtained are greater, allowing lower detection limits to be achieved and enabling the technique to be extended to less volatile compounds.

SUMMARY

Thermal desorbtion is an extremely useful means of injecting samples collected on sorbent traps into a gas chromatograph for analysis. It eliminates the use of solvents, and requires less handling, is more sensitive, and less costly than solvent desorbtion. TEKMAR's new Model 5000 Automatic Desorber combines innovative new features with powerful microprocessor control to produce outstanding performance for the analysis of sorbent traps. The Desorber is applicable to monitoring of ambient air, stack gases, and industrial hygiene analysis.

References:

1) Berkley, R.E., Bumgarner, J.E., Driscoll, D.J., Morris, C.M., and Wright, L.M., "Standard Operating Procedure for the GC/MS Determination of Volatile Organic Compounds Collected on Tenax". U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, EMSL/RTP-SOP-EMD-021, June 27, 1984

TABLE 1: RECOVERIES OF VOLATILE ORGANIC COMPOUNDS BY ACTIVE VS PASSIVE DESORBTION

Compound	Active Desorb	Passive Desorb
Perflourotoluene	104%	96%
Toluene	95%	76%
Chlorobenzene	95%	68%
Ethylbenzene	95%	63%
o-Xylene	94%	58%
p-Chlorotoluene	80%	46%
1,2,4-Trichlorobenzene	80%	42%

TABLE 2: ANALYTICAL CONDITIONS

Trap:	5/8" X 7" SS Tenax
Prepurge:	2 min. at 10ml/min.
Internal Trap:	1/16" open bore, -100°C
Desorb:	8 min. at 10ml/min., 190°C
Transfer:	1 min. at 250°C
Cryofocus:	-100° Inject: 0.5 min @ 250°
Valve:	270° Line: 210° Injector: 200°
GC Column:	25m x 0.32mm fused silica, 1 micron SE-54
Program:	45° for 2 min., 6°/min. to 200°
Carrier:	Hydrogen at 50cm/s
Detector:	FID, range 10^{-12}, attn. as marked

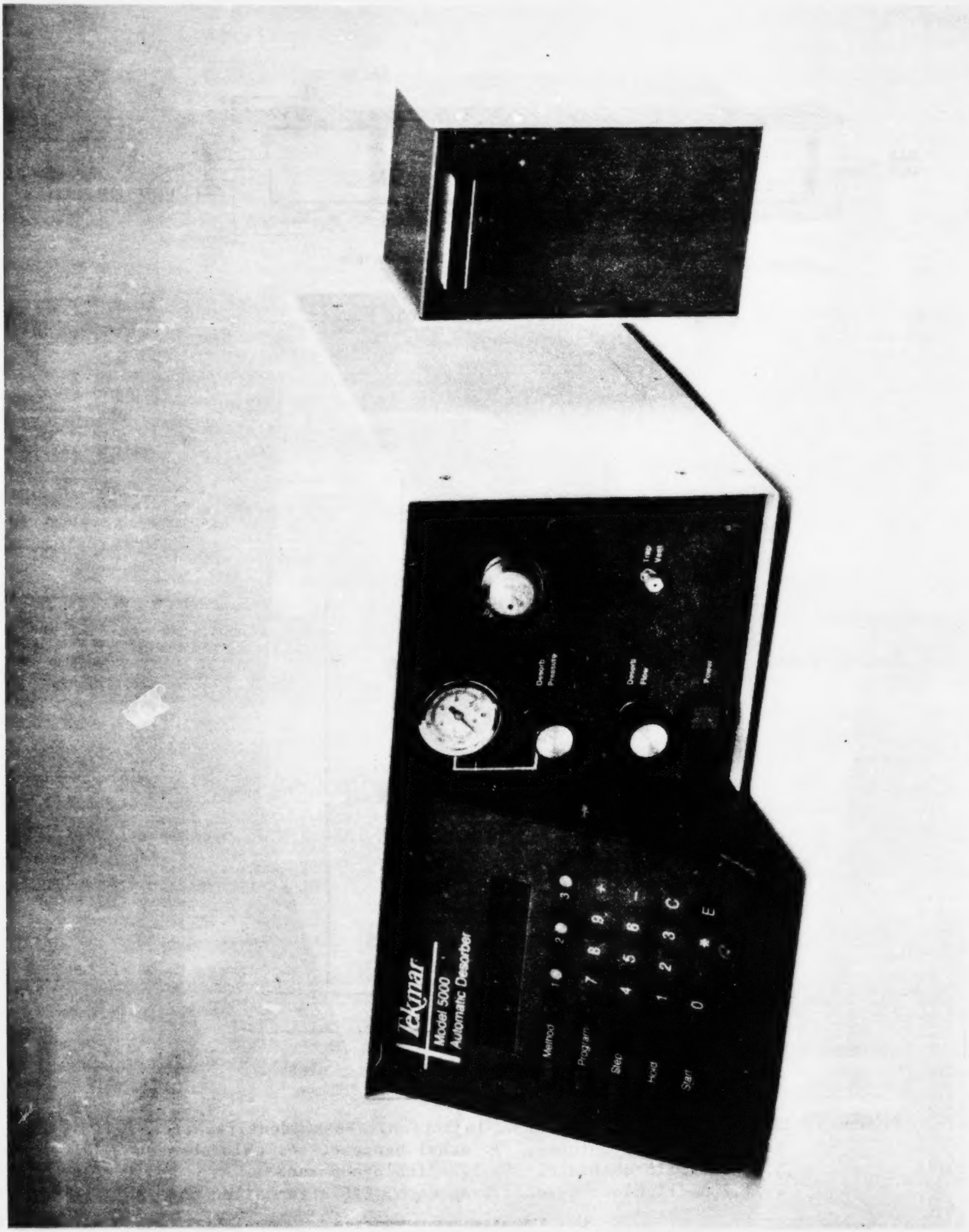

Tekmar
Model 5000
Automatic Desorber
Method
Program
Step
Hold
Start
1 2 3
7 8 9 +
4 5 6 −
1 2 3 C
0 * E
Desorb Pressure
Desorb Flow
Power
Trap Vent

FIGURE 1

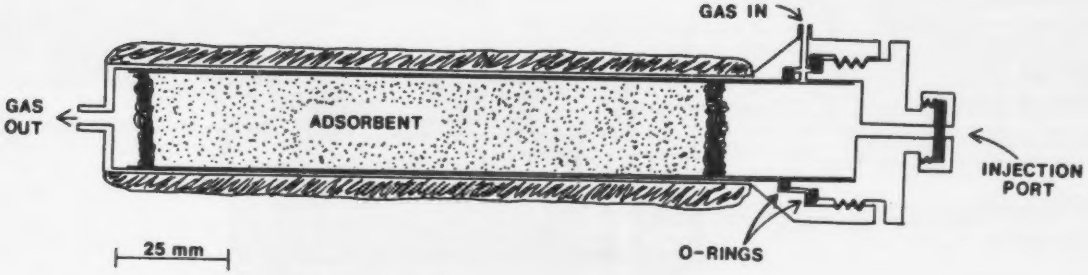

GAS IN
GAS OUT
ADSORBENT
INJECTION PORT
O-RINGS
25 mm

Figure 2: Cutaway view of tube heater

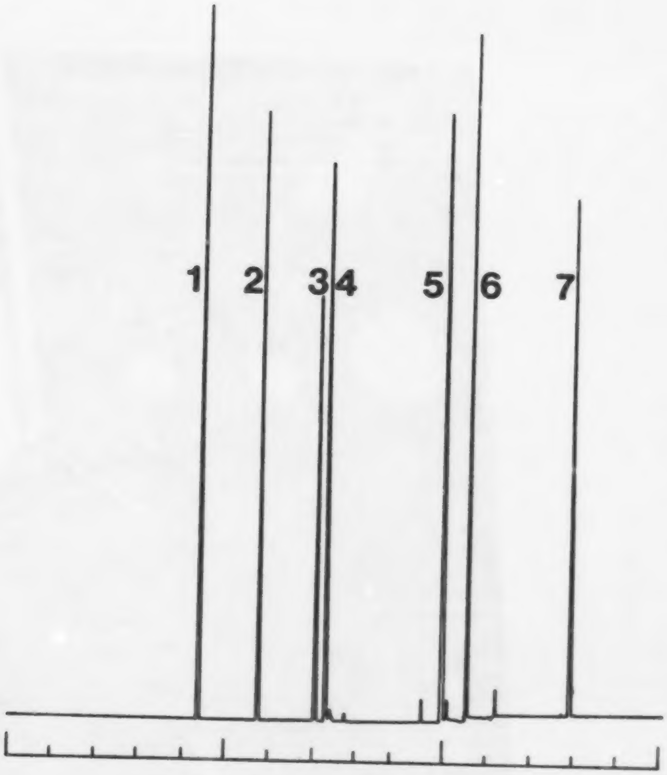


Figure 3: Chromatogram of focussed GC injection. Peak Identifications:
1: benzene, 2: toluene, 3: ethyl benzene, 4: chlorobenzene
5: 1,3-dichlorobenzene, 6: 1,2-dichlorobenzene
7: 1,2,4-trichlorobenzene, 6 ng each, FID attenuation 64.

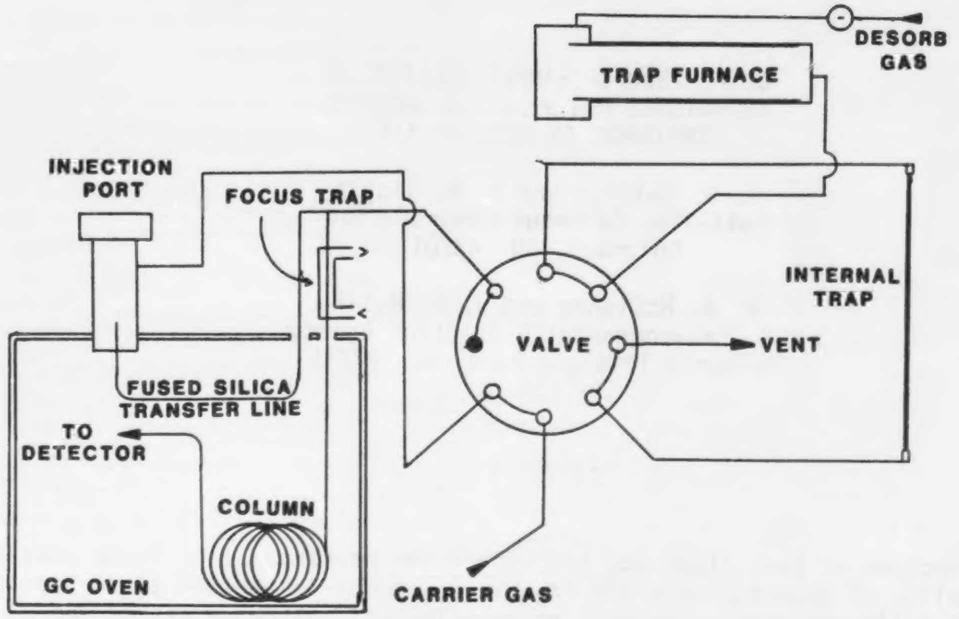

DESORB GAS
TRAP FURNACE
INJECTION PORT
FOCUS TRAP
INTERNAL TRAP
VALVE
VENT
FUSED SILICA TRANSFER LINE
TO DETECTOR
COLUMN
GC OVEN
CARRIER GAS

Figure 4: Gas Flow System

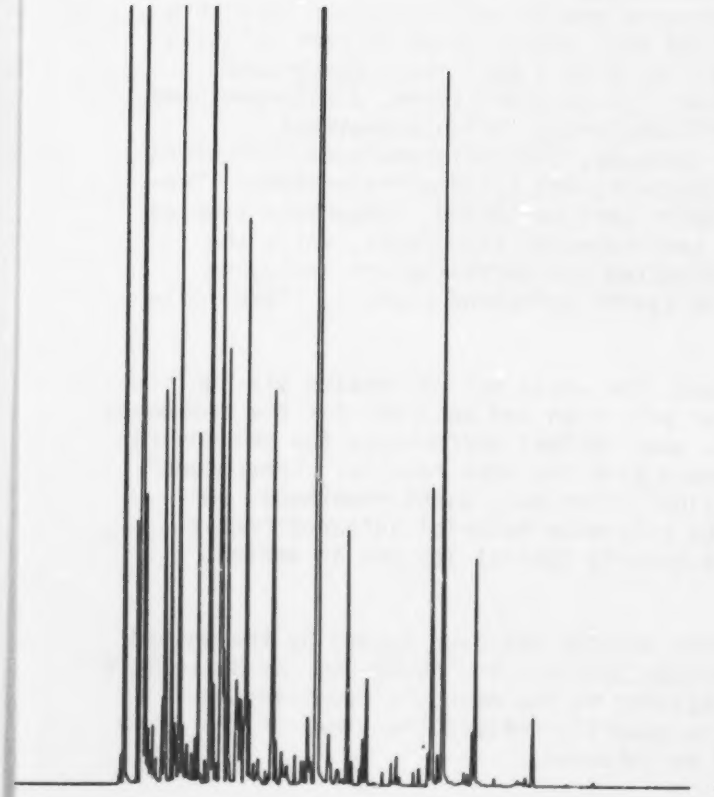


Figure 5:
Chromatogram of 10 liters ambient air sampled on Tenax, FID attenuation 512.

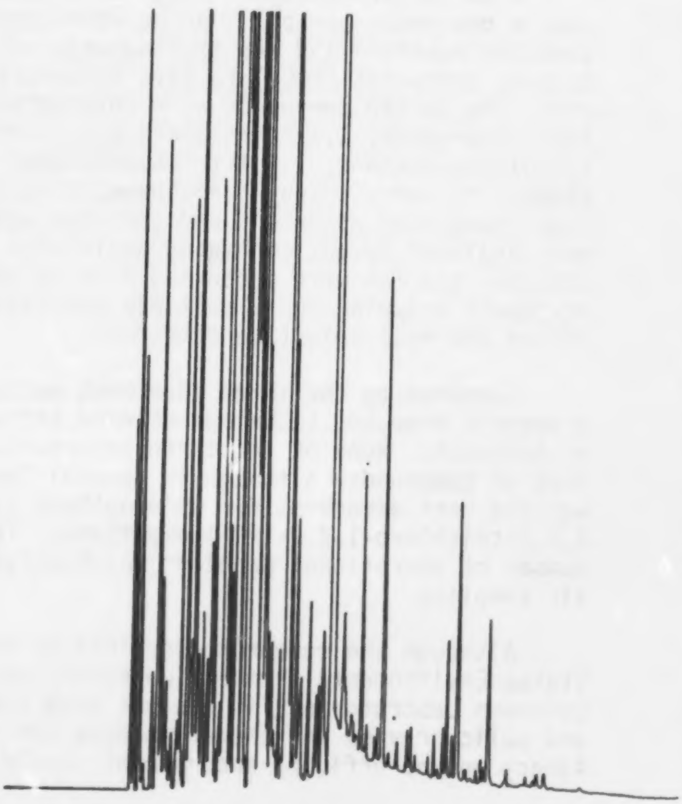


Figure 6:
Chromatogram of 10 liters indoor air sampled on Tenax, FID attenuation 512.

COMPARISON OF SAMPLE COLLECTION TECHNIQUES FOR VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

M. W. Holdren and R. M. Riggin
Battelle, Columbus Laboratories
Columbus, OH 43201

W. A. McClenny and J. D. Mulik
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

ABSTRACT

The objective of this study was to compare the performance of techniques for the sampling of selected volatile organic compounds in ambient air. Specifically, three solid adsorbents (Tenax®, an experimental polyimide resin, and Spherocarb®) were examined along with a whole air collection by SUMMA® treated canisters.

A series of 10 experimental sampling runs were conducted at a field site over a one-month period. During each experiment ambient air was drawn through a sampling manifold and was continuously spiked with a mixture of fifteen volatile organic compounds (VOCs) to give concentrations 1 to 3 ng/l above background air. The spiked compounds were chloroethene, 1,1-dichloroethene, dichloromethane, 3-chloropropene, 1,1,2-trichloro-1,2,2-trifluoroethane, trichloromethane, 1,2-dichloroethane, 1,1,1-trichloroethane, benzene, tetrachloromethane, trichloroethene, toluene, tetrachloroethene, chlorobenzene, and 1,2-dimethylbenzene. Two-hour integrated adsorbent and canister samples were collected. Adsorbent samples were analyzed by gas chromatographic/mass spectrometric techniques, while the canister samples were processed with an automated gas chromatograph employing cryogenic trapping and a multiple detection system (electron capture, flame ionization and mass selective detectors).

Compared to the three adsorbent methods, the whole air collection via canister cryogenic trapping technique offered better precision and accuracy for the compounds of interest. None of the three adsorbents gave optimal performance for the entire list of compounds, although in general Tenax® gave the best results. Spherocarb® was the best adsorbent for chloroethene (vinyl chloride), dichloromethane, and 1,1,2-trichloro-1,2,2-trifluoroethane. The polyimide material suffered from a number of operational problems which weigh heavily against its use in ambient air sampling.

Although the research described in this article has been funded by the United States Environmental Protection Agency through Contract No. 68-02-3487 by Battelle's Columbus Laboratories, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

INTRODUCTION

The Methods Development and Analysis Division of the Environmental Monitoring Systems Laboratory (EMSL) of the U.S. Environmental Protection Agency is responsible for the development and evaluation of state-of-the-art and emerging analytical techniques for the determination of organic compounds in ambient air. Recently a priority listing of volatile organics has been established and EMSL is focusing on further development of analytical methodology for the determination of these compounds.

In general one of two approaches, whole air collection into specially treated canisters or selective collection by solid adsorbents is used to sample volatile organics in ambient air. By far the most widely employed adsorbent for volatile organic compounds is Tenax® GC. Tenax® has the advantage of good thermal stability which allows for efficient desorption of higher boiling compounds (e.g., C-12 hydrocarbons) during the analysis step. A primary limitation of Tenax® is the low retention volume of highly volatile compounds (e.g., vinyl chloride, 1,2-dichloroethane, etc.). In order to extend the applicability of solid adsorbent collection to more volatile compounds, EMSL has conducted development and evaluation studies for various adsorbents which could be used in place of, or in combination with Tenax®. The two most promising materials for this purpose are (1) a polyimide material formed from pyromellitic anhydride and 4,4'-diaminodiphenylsulfone, and (2) carbon molecular sieves (CMS) sold under the tradenames Spherocarb®, Carbosieve®, or Carbosphere®.

The specific objective of the work described here was to compare the performance of the three adsorbents (Tenax®, polyimide, and Spherocarb®) as well as canister collection for sampling and analysis of representative volatile organic compounds at realistic concentrations in ambient air.

PROCEDURES

Three adsorbents--Tenax®, polyimide, and Spherocarb®, as well as whole air collection into canisters were operated in parallel to sample ambient air, using the sampling manifold shown in Figure 1. The air stream was spiked with 1-3 ng/liter levels of each target compound in order to ensure the presence of a detectable concentration.

Whole air sampling was accomplished by collecting integrated samples, over the entire two-hour sampling period, using specially treated stainless steel canisters. A sample volume of 500 ml was taken from each canister and analyzed by cryogenic trapping/gas chromatography using flame ionization, electron capture, and mass selective detectors. Compound separation was facilitated with a 50 meter wide-bore fused silica capillary column (OV-1). The individual compounds were eluted using a temperature program of -70°C to 150°C at 8°/minute.

Duplicate ten-liter samples were collected using each of the three adsorbents. In addition five and twenty-liter samples were collected using Tenax®. All adsorbent samples were analyzed by gas chromatography/mass spectrometry. The analytes were thermally desorbed from the cartridges onto a liquid nitrogen-cooled trap and subsequently transferred onto a wide-bore fused silica capillary column. The individual compounds were eluted using a temperature program of -70°C to 150°C at 8°/minute. Components were quantified by comparing the integrated ion intensity for a characteristic ion of each compound to that of standard injected on the same day.

More details on the experimental portion of the program may be found elsewhere (1,2).

RESULTS AND DISCUSSION

An estimate of the analytical precision of the various sampling and analytical methods was determined from replicate analyses of canister and adsorbent samples. Due to the limitation in software only six compounds could be monitored in real-time with the mass selective detector. As a result, replicate analyses were only performed on six of the fifteen compounds with samples from the canisters. Table 1 shows the estimate of precision for these six compounds using all four collection techniques. It is evident that, in general, the canister collection technique offers somewhat better precision.

Data on method accuracy were obtained by flowing a known calibration mixture through the sampling manifold and determining percent recovery of each compound per method. The results are shown in Table 2. Again the canister sampling technique gave the best performance. Recoveries with this technique ranged from 89 to 120 percent for the fifteen target compounds (excluding 1,1,2-trichloro-1,2,2-trifluoroethane). Tenax®, which overall showed the best compound recovery for the adsorbents, gave values that ranged from 8 to 104 percent (excluding dichloromethane).

In order to compare the performance of the various methods for ambient air, the apparent recovery of the adsorbent samples for each run was calculated, relative to the value obtained from the analysis of the canister. Use of the canister value was considered to be most appropriate since this technique generally agreed best with the concentration in the calibration cylinder, and gave better overall precision than did any of the adsorbent techniques. Most of the values used for the canister data were obtained using the mass selective detector, since this detection system was less subject to potential interferences. However, the toluene and 1,2-dimethylbenzene values were obtained using flame ionization detection due to limitations on the number of ions which could be monitored using the mass selective detector.

An example of the performance of Tenax® relative to canister collection for the compound benzene is shown in Figure 2. After correcting for the outlier data point, a relative recovery of 114 percent is obtained. Comparative data for the various adsorbents relative to canister sampling is summarized in Table 3. For poorly retained compounds the low volume Tenax® sample (nominally 5 liters) was used, whereas for better retained compounds the average of duplicate 10 liter Tenax® samples was used.

As expected, none of the adsorbents performed well for all of the target compounds. Tenax® performed best for 3-chloropropene, trichloromethane, 1,2-dichloroethane, 1,1,1-trichloroethane, benzene, tetrachloromethane, trichloroethene, tetrachloroethene, chlorobenzene, and 1,2-dimethylbenzene. Tenax® and polyimide gave essentially identical results for toluene. As expected, on the basis of breakthrough volume data, Tenax® gave essentially no recovery for chloroethene (vinyl chloride) and 1,1-dichloroethene (vinylidene chloride).

Polyimide performed better than both Spherocarb® and Tenax® only for 1,1-dichloroethene, although only 55 percent recovery and 28 percent standard deviation were obtained. Polyimide gave essentially no recovery for chloroethene, in spite of the good recovery obtained for this compound in high purity air sampling (2). Polyimide also gave disappointingly low and variable recovery for 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113), 1,1,1-trichloroethane, and tetrachloromethane. An operational problem which weighs heavily against the use of this material for ambient air sampling is the adsorption of a significant amount of moisture onto the adsorbent. The presence of water in the matrix led to the chromatographic column plugging during virtually all of the ambient air sampling runs. A similar phenomenon is observed for Spherocarb®. However, in that case the cartridge is prepurged with dry air at room temperature prior to analysis, to remove adsorbed moisture. A similar approach was not successful in eliminating the problem for the polyimide material, indicating that the collected moisture is difficult to desorb due to kinetic or thermodynamic factors.

Spherocarb® gave the best results of the three resins only for chloroethene, dichloromethane, and 1,1,2-trichloro-1,2,2-trifluoroethane. Spherocarb® gave extremely poor results for 1,1-dichloroethene, 3-chloropropene, 1,2-dimethylbenzene, and tetrachloromethane. In the case of 1,1-dichloroethene artifactually high recovery, possibly due to dehydrohalogenation of 1,1,1-trichloroethane, was a major problem. Although low recoveries were anticipated for the other three compounds, on the basis of earlier work, the low recovery of 1,1-dichloroethene was not observed previously (3).

In spite of the problems discussed above, the data set is somewhat encouraging in terms of the implications for ambient air sampling. Inspection of the raw data reveals that, except for the major problem areas discussed above, the individual values generally agree with the values obtained from canister sampling within a factor of two or better (i.e., 50 to 150 percent relative recovery).

CONCLUSIONS AND RECOMMENDATIONS

Compared to the three adsorbent methods tested, whole air collection via canisters results in better precision for the compounds of interest in this study. An estimate of precision (% standard deviation) for the canister sampling method ranged from 4 to 10 percent. For Tenax®, which gave the best performance for the adsorbents, precision values ranged from 8 to 16 percent. Data on recovery of the target compounds in the spiked manifold clearly indicate better accuracy with the canister sampling procedure. When comparing measured recoveries with expected concentrations, the canister sampling approach yielded values from 89 to 120 percent. Recoveries, using Tenax® adsorbent, ranged from 8 to 104 percent.

Additional studies should be undertaken under controlled conditions with analytical uncertainties minimized as much as possible by employing the same analysis procedure for all collected samples. Sampling techniques to be compared should include distributive air volume sampling with Tenax® adsorbent, passive sampling using personal exposure devices, and whole air collection in canisters.

REFERENCES

(1) Holdren, M. W., Smith, D. L., and R. N. Smith. Field Evaluation of An Automated Cryogenic Preconcentration and Gas Chromatographic System. Contract No. 68-02-3487 (WA-37). U.S. Environmental Protection Agency, Research Triangle Park, NC, January, 1985.

(2) Riggin, R. M. and Markle, R. A. Comparison of Solid Adsorbent Sampling Techniques for Volatile Organic Compounds In Ambient Air. Contract No. 68-02-3487 (WA-31). U.S. Environmental Protection Agency, Research Triangle Park, NC, January, 1985.

(3) Riggin, R. M. Evaluation of Carbon Molecular Sieves As Adsorbents for the Determination of Volatile Organic Compounds. In: Proceedings of Quality Assurance in Air Pollution Measurements, Air Pollution Control Association, Boulder, CO, October, October, 1984, pp. 14-18.

TABLE 1. ANALYTICAL PRECISION DATA FROM REPLICATE ANALYSES OF SOLID ADSORBENT AND CANISTER SAMPLES[(a)]

Compound	Canister Collection	Tenax®	Polyimide	Spherocarb®
Trichlorotrifluoroethane	10.1	11.8	39.0	9.8
Trichloromethane	7.3	7.8	13.5	27.8
1,1,1-Trichloroethane	8.7	8.0	18.1	19.1
Tetrachloromethane	6.4	16.0	26.4	27.9
Trichloroethylene	7.3	14.3	15.6	18.3
Tetrachloroethene	4.0	11.8	8.9	28.4

(a) Precision = % Standard Deviation.

TABLE 2. RESULTS FOR CALIBRATION CYLINDER SAMPLING EXPERIMENT

Compound	Expected Concentration, ng/L	Percent Recovery(a)			
		Canister Collection	Tenax®	Polyimide	Spherocarb®
Chloroethene(b)	26	103	8.3	79	58
1,1-Dichloroethene(b)	17	112	55	91	76
Dichloromethane(b)	13	107	360	119	100
3-Chloropropene(b)	19	95	79	66	60
1,1,2-Trichloro-1,2,2,-Trifluoroethane(b)	34	230	47	60	123
Trichloromethane(b)	27	100	104	85	93
1,2-Dichloroethane(b)	24	120	96	40	63
1,1,1-Trichloroethane(b)	30	117	89	107	75
Benzene	15	93	73	115	105
Tetrachloromethane(b)	36	103	89	118	64
Trichloromethane	27	89	76	87	93
Toluene	18	90	50	65	52
Tetrachloroethene	34	118	65	68	76
Chlorobenzene	22	118	43	47	33
1,2-Dimethylbenzene	20	120	23	28	13

(a) Average for duplicate samples.

(b) Low volume (nominally 5 liters) Tenax® value used for these compounds. Medium volume (nominally 10 liters) Tenax® value used for all other compounds.

TABLE 3. PERFORMANCE DATA FOR SOLID ADSORBENTS RELATIVE TO CANISTER SAMPLING

Compound	Tenax® Breakthrough Volume(a), Liters/Cartridge	Average Recovery Relative To Canister Sampling, %		
		Tenax®	Polyimide	Spherocarb
Chloroethene	0.8	--(b)	--(b)	73(23)(d
1,1-Dichloroethene	Not Given	--(b)	52(28)	410(260)
Dichloromethane	4	83(21)	86(31)	85(12)
3-Chloropropene(c)	6	87(35)	140(68)	29(14)
1,1,2-Trichloro-1,2,2-Trifluoroethane	Not Given	39(25)	17(14)	69(30)
Trichloromethane(c)	13	100(36)	75(25)	65(17)
1,2-Dichloroethane(c)	18	100(15)	65(15)	75(14)
1,1,1-Trichloroethane(c)	9	130(42)	51(14)	46(10)
Benzene	27	110(18)	130(34)	140(63)
Tetrachloromethane(c)	13	110(37)	53(19)	29(9)
Trichloroethene	28	112(26)	100(33)	90(33)
Toluene	122	70(19)	70(17)	43(8)
Tetrachloroethene	106	88(27)	78(30)	72(30)
Chlorobenzene	249	78(35)	57(21)	53(19)
1,2-Dimethylbenzene	334(e)	55(21)	40(15)	20(7.9)

(a) Data from Reference 2 at 90°F.

(b) No meaningful data obtained.

(c) Low volume (nominally 5 liters) Tenax® value used for these compounds. Medium volume (nominally 10 liters Tenax® value used for all other compounds.

(d) Value in parentheses is standard deviation for all sampling runs.

(e) Value for ethylbenzene.

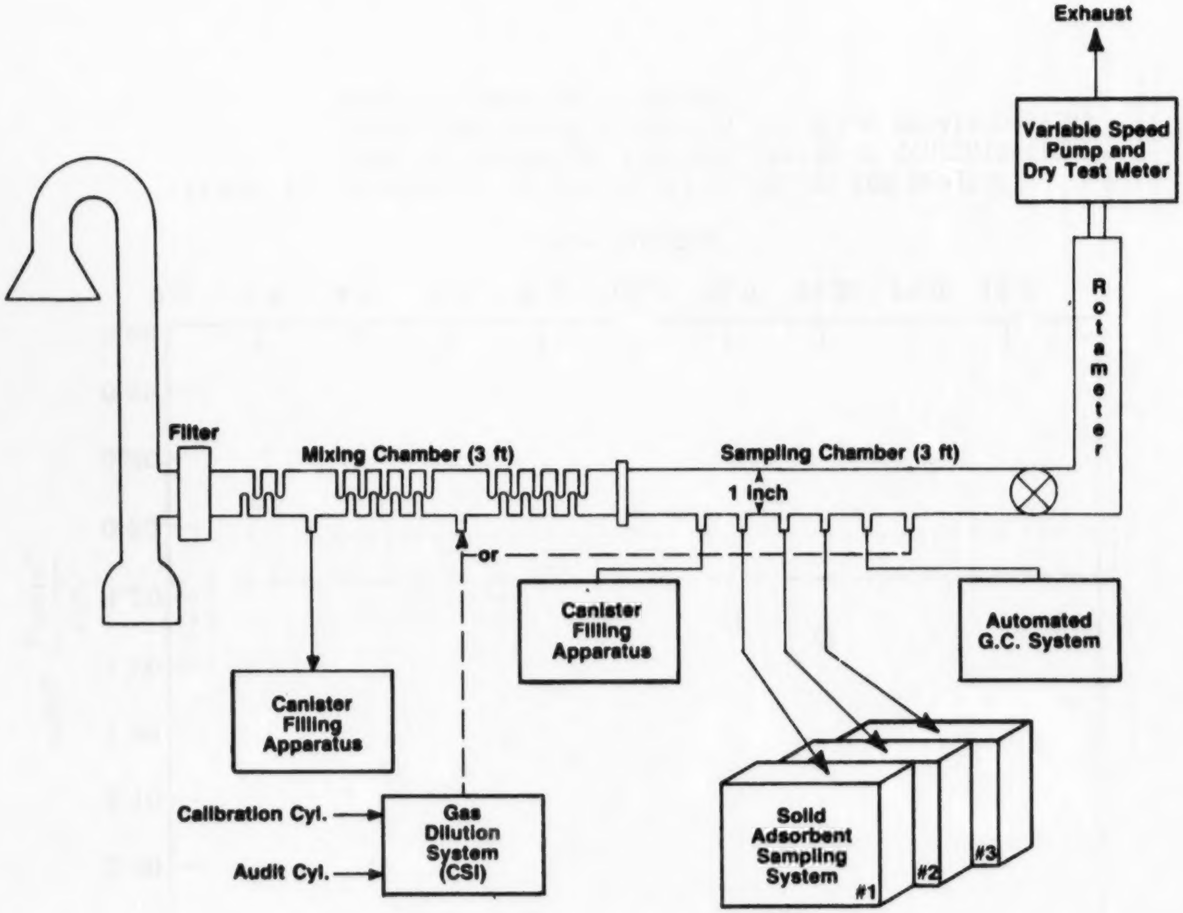

Exhaust
Variable Speed Pump and Dry Test Meter
Rotameter
Filter
Mixing Chamber (3 ft)
Sampling Chamber (3 ft)
1 inch
or
Canister Filling Apparatus
Automated G.C. System
Canister Filling Apparatus
Calibration Cyl.
Audit Cyl.
Gas Dilution System (CSI)
Solid Adsorbent Sampling System
#1
#2
#3

FIGURE 1. GLASS MANIFOLD USED DURING AIR SAMPLING PROGRAM

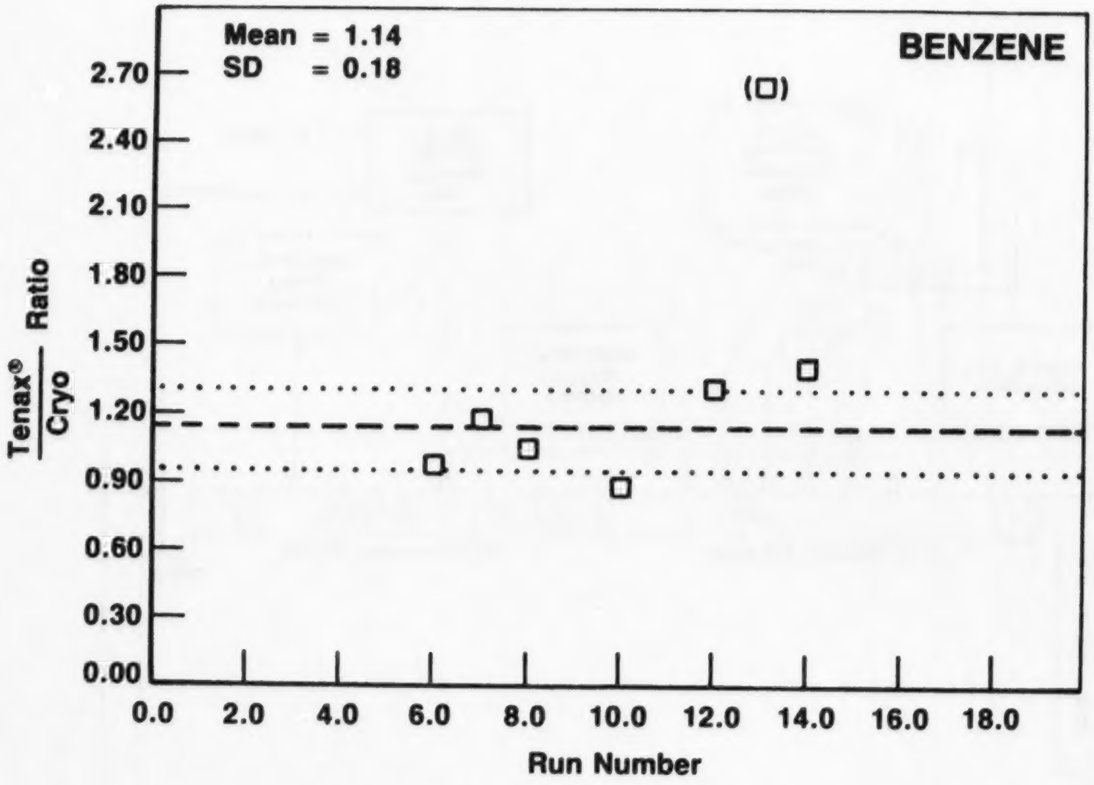


FIGURE 2. SCATTERPLOT OF CONCENTRATION RATIOS FOR BENZENE FROM SPIKED AMBIENT AIR RUNS (RATIO IS CONCENTRATION VALUE FROM TENAX® DIVIDED BY THE VALUE OBTAINED USING CANISTER SAMPLING TECHNIQUE)

BENZENE AND TOLUENE CONCENTRATIONS IN LAKE CHARLES, LOUISIANA AMBIENT AIR

Dennis M. Casserly
University of Houston-Clear Lake
Houston, Texas 77058

Kenneth K. O'Hara
McNeese State University
Lake Charles, Louisiana 70609

INTRODUCTION

The concentration of volatile organic compounds (VOC's) in ambient air is primarily of interest because of their involvement in the formation of photochemical smog. However, among the vapor phase components, there also exist mutagenic and potentially carcinogenic vapors (Krost et al, 1982). The petrochemical industries and related activities are generally assumed to be the major sources of VOC's in ambient air. Significant sources that have contributed to the degradation of urban air quality include: waste lagoons (Shen, 1982); activated sludge treatment plants (Lurker et al, 1982); chemical waste sites (Pellizarri, 1982); and automobiles (Pilar and Graydon, 1973). Ubiquitous background sources are animal and plant matter, forest and grass fires and seepage of crude oil (Brief et al, 1980). Atlas and Giam (1981) have found VOC's in remote regions of the North Pacific marine atmosphere implying a global distribution and transport for some refractory compounds.

A large number of VOC's have been regularly found in urban centers throughout the world: 20 mutagenic VOC's in seven U.S. cities by Singh et al (1983); 25 VOC's at three urban sites in New Jersey by Harkov et al (1983); 22 halogenated hydrocarbons in Louisiana by Pellizarri (1982); and 48 VOC's regularly found in Sydney, Australia by Nelson and Quigley (1982), which they estimated contributed to 90% of the non-methane hydrocarbons measured.

North of Lake Charles are pine plantations and to the south are salt marshes both of which are seasonally burned to control undesirable plant growth. Throughout the area are oil and gas fields. In the greater Lake Charles area are chemical industries, refineries, hazardous waste sites and motor vehicle activity all of which would contribute to a complex chemical mixture in the ambient air.

The purpose of this project was to provide a baseline study of the volatile organics benzene and toluene in ambient air at two distinct sampling locations, one near the center of industrial and urban activity and the other remote and generally upwind from such areas.

METHODS

Samples were collected from January through December 1983 at existing sites established by the Louisiana Department of Natural Resources. The stations are part of EPA's network of State and Local Air Monitoring Stations (SLAMS).

Air samples were collected according to ANSI/ASTM (1979) procedure D-1605-60, Standard Recommended Practices for Sampling Atmospheres for Analysis of Gases and Vapors,and procedure D-3686-78, Standard Practice for Sampling Atmospheres to Collect Organic Compound Vapors. A vacuum pump was used to move air through a coconut charcoal tube (100/50 mg, 20/40 mesh). Sampling occurred for a 24 hour period at a flow rate of one liter per minute, maintained by a critical orifice. Flow rate was calibrated before and after each sample collection using a 100 ml bubble flow meter. The collection tubes were kept verticle to prevent channeling. After sampling, the tubes were capped and returned to the laboratory for desorption and analysis.

Analyses were performed according to ANSI/ASTM method D-3686-78, Standard Practices for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Method (1979). Front and back charcoal sections were placed in separate vials with teflon caps and desorbed with 0.5 ml carbon disulfide. Sample vials were agitated for 30 minutes for desorption to occur. A gas chromatograph with a flame ionization detector was used for analysis. The column was 20' x 1/8" stainless steel with 10% SP-1000 on 80/100 Supelcoport. Chromatographic conditions were programmed for maximum separation of sample components. Analyses were conducted in triplicate.

RESULTS AND DISCUSSION

The procedures employed were adequate to quantify low concentrations of benzene and toluene in 53 samples analyzed. All field blanks were negative and no sample showed breakthrough. Data were corrected for temperature and pressure and reported for standard conditions (0°C and 760 mmHg). Olson et al (1983) found the charcoal technique suitable for quantitative determination of eight organics which included benzene and toluene. According to Kring et al (1984), the method has a precision of 5% relative standard deviation at 95% humidity. Levine and Schneider (1982) found sample recoveries to be greater at flow rates of 2 liters per minute than at lower flow rates of 0.2 liters per minute, presumably due to turbulent flow that increases adsorption efficiency. Sampling time showed no effect on recoveries but high organic loads on the charcoal resulted in breakthrough.

In this study, both benzene and toluene concentrations were observed to follow log-normal distributions. Although both compound concentrations were slightly higher at the industrial site than the upwind site, paired t-test results indicated no significant differences ($p>0.05$) in concentrations between the two sites. The geometric mean and geometric standard deviation for benzene was 6.6 ± 1.7 ug/M^3 with 10% of the values exceeding 14.5 ug/M^3. The toluene concentrations averaged 5.5 ± 1.7 ug/M^3 with 10% of the values exceeding 12.3 ug/M^3. Slightly higher concentrations of both compounds were noted during the summer months presumably due to increased volatile losses during warm temperature periods. Toluene and benzene concentrations were positively correlated ($r = 0.60$) with an average ratio of 0.87:1.

Sievers _et al_ (1980) reported global background averages of 0.6 - 6.4 ug/M^3 for benzene and 4.5 - 19 ug/M^3 for toluene. Concentrations observed at industrial and urban centers tend to be higher. Harkov _et al_ (1983) found average values of 3.4 ug/M^3 for benzene and 6.8 - 17.5 ug/M^3 for toluene in New Jersey. Nelson and Quigley (1982) reports benzene concentrations of 8.2 ug/M^3 and toluene concentrations of 33.4 ug/M^3 in Sydney, Australia. In Toronto, Pilar and Graydon (1973) measured benzene concentrations at 41 ug/M^3 and toluene concentrations of 113 ug/M^3.

The levels of benzene and toluene in the Lake Charles area ambient air were within the ranges found in other parts of the world. There appears to be no significant difference between the industrial and the upwind site, indicating no significant point sources of benzene and toluene in the area but rather common diffuse sources.

REFERENCES

1. Atlas, E. and C. S. Giam, "Global Transport of Organic Pollutants: Ambient Concentrations in the Remote Marine Atmosphere," _Science_, Vol.211, No.9 (1981).

2. Brief, R. S., J. Lynch, T. Bernath and R. A. Scala, "Benzene in the Workplace," American Industrial Hygiene Association Journal, No.41, September (1980).

3. Harkov, R., B. Kebbekus, J. W. Bozzelli and P. K. Lioy, "Measurement of Selected Volatile Organic Compounds at Three Locations in New Jersey During the Summer Season," Journal of the Air Pollution Control Association, Vol. 33, No.112 (1983).

4. Kring, E. V., G. R. Ansul, T. J. Henry, J. A. Morello, S. W. Dixon, J. F. Vasta and R. E. Hemingway, "Evaluation of the Standard NIOSH Type Charcoal Tube Sampling Method for Organic Vapors in Air," American Industrial Hygiene Association Journal, Vol.45, No.4 (1984).

5. Krost, K. J., E. D. Pellizzari, G. S. Walburn and S. A. Hubbard, "Collection and Analysis of Hazardous Organic Emissions," Analytical Chemistry, Vol. 54, 810 (1982).

6. Lurker, P. A., C. S. Clark and V. J. Elia, "Atmosphereic Release of Chlorinated Organic Compounds from the Activated Sludge Process," Journal of the Water Pollution Control Federation, Vol.54, No.12 (1982).

7. Nelson, P. F. and S. M. Quigley, "Non-Methane Hydrocarbons in the Atmosphere of Sydney, Australia," Environmental Science and Technology, Vol.16, No.10 (1982).

8. Olson, R., D. T. Williams, and P. D. Bothwell, "Charcoal Tube Technique for Simultaneous Determination of Selected Organics in Air," American Industrial Hygiene Association Journal, Vol.44, No.7 (1983).

9. Pellizzari, E. D., "Analysis for Organic Vapor Emissions Near Industrial and Chemical Waste Disposal Sites," Environ. Sci. Technol., Vol.16, No.11 (1982).

10. Pilar, S. and W. F. Graydon, "Benzene and Toluene Distribution in Toronto Atmosphere," Environ. Sci. Technol., Vol.7, No.7 (1973).

11. Shen, T. T., "Estimation of Organic Compound Emissions From Waste Lagoons," Journal of the Air Pollution Control Association, Vol.32, No.1 (1982).

12. Sievers, R. E., R. M. Barkley, D. W. Denney, S. D. Harvey, J. M. Roberts, M. J. Bollinger and A. C. Delaney, "Gas Chromatographic and Mass Spectrometric Analysis of Volatile Organics in the Atmosphere," Sampling and Analysis of Toxic Organics in the Atmosphere, ASTM STP 721 (1980).

13. Singh, H. B., L. J. Salas and R. E. Stiles, "Distribution of Selected Gaseous Organic Mutagens and Suspect Carcinogens in Ambient Air," Environ. Sci. Technol. Vol.16, No.12 (1982).

DETERMINATION OF 2-DIETHYLAMINOETHANOL IN AIR

Michael R. Whitbeck
Associate Research Professor
Desert Research Institute, University of Nevada System, Reno, NV

ABSTRACT

The extensive use of 2-diethylaminoethanol (DEAE) provides the potential for human exposure from polyurethane foams, humidifier, etc. In this paper an ion-exchange chromatographic procedure for determining DEAE concentration in air is presented that overcomes difficulties associated with existing methods.

INTRODUCTION

2-Diethylaminoethanol (DEAE) is widely used in industry as a solubilizer, emulsifier, anticorrosion additive to boilers, sterilizers and food processing equipment, as a photoactivator and in epoxy resin formulations. Because of this extensive use, the potential for human exposure to 2-diethylaminoethanol and its degradation products as air contaminants exists(1,2,3) and there is a need for a simple and rapid method to determine its concentration in air.

Colorimetric methods for analysis of DEAE in air have been used based on oxidation of the aminoalcohol by dichromate(3) or hypochlorite(4). Derivatization of the aminoalcohol to form a colored product has also been used(3,5), and a gas chromatography method has been described(6). These methods require very large sample volumes, suffer from extensive sample preparation and extraction steps, or lack the desired specificity for ambient air analysis. In this paper, an ion chromatographic method for determining DEAE concentrations in air will be presented that overcomes the difficulties associated with the existing methods.

EQUIPMENT AND MATERIALS

In this paper all water used was 18 megohm deionized water from a Waters Associates Milli-Q water system. The DEAE was Aldrich Gold Label (99+% pure). The chromatography was performed using a Dionex System 14 IC with a 0.5 ml sample loop and 0.005 N hydrochloric acid as the eluent at a flow rate of 150 ml/hr. The chromatograph was equipped with a cation concentrator column (#030830), a separation column (#030831), and a suppressor column (#030834).

EXPERIMENTAL

A calibration curve was made by diluting DEAE with deionized water to form solutions of 1-20 ppmm DEAE. These solutions gave a linear increase in peak height and peak area as a function of concentration in the 5-20 ppmm range (Figure 1). Ammonia and amines at low concentrations typically give such a nonlinear response in ion chromatography using a conductance detector. Although this may be corrected by adding a chloride postcolumn, in this study the concentrations were kept in the linear range of Figure 1.

To test the trapping efficiency of water impingers for DEAE a gas phase sample was prepared by injecting 1.6 microliters/hr of DEAE with a syringe pump into nitrogen flowing at 0.4 lpm to produce a DEAE concentration of 59 mg/m^3 +/- 20%. This test stream was sampled by two microimpingers in series. Each microimpinger contained 10 ml of deionized water and was sampled for 9 minutes. The high solubility of

DEAE in water combined with the short sampling times permits the use of deionized water as the trapping media in place of dilute acid(5). Analysis of the first impinger gave a value of 17 ppmm. The 17 ppmm corresponds to a gas phase DEAE concentration of 47 mg/m^3 and is within the expected accuracy for the syringe pump. No DEAE was detected in the second impinger.

DISCUSSION

The determination of 2-diethylaminoethanol in air by ion chromatography offers two significant advantages over existing methods, first is the use of a simple water impinger for sampling, and second, there is no need for derivatization or extraction steps. A typical chromatogram is shown in Figure 2. The two small peaks after the water dip are from sodium and ammonium cations present as trace impurities. These ions elute at much shorter times than DEAE and thus do not interfere with the method.

The principal disadvantage is the nonlinear response at low concentrations of DEAE. This presents a minor difficulty that may be overcome by taking somewhat larger samples so that the aqueous aminoalcohol concentration falls in the linear response region.

REFERENCES

(1) P. Pryor, Health Hazard Evaluation Report, HETA 80-148-1025, NIOSH, May (1980).

(2) K.P. McManus, Health Hazard Evaluation Report, HETA 81-247-958, NIOSH, Sept. (1981).

(3) F.A. Miller, R.F. Scherberger, K.S. Tischer, and A.M. Weber, Determination of Microgram Quantities of Diethanolamine, 2-methylaminoethanol, and 2-diethylaminoethanol in Air, Am Ind. Hygiene Assoc. J., 28, 330-334 (1967).

(4) O.N. Putilina, and N.T. Yarym-Agavera, Photometric Method for the Determination of Tertiary Fatty Amines and Aminoalcohols in the Air, Gig. Tr. Prof. Zabol., 7, 55-57 (1981).

(5) E.N. Pomozova, and N.F. Volokhova, Determination of Diethylaminoethanol in the Air, Uch. Zap. Mosk. Nauchno Isslad. Inst. Gig., 22, 172-173 (1975).

(6) G.O. Wood and J.W. Nickols, Development of Air Monitoring Techniques Using Solid Sorbents, LASL Report LA-7295-PR, NIOSH-IA-77-12.

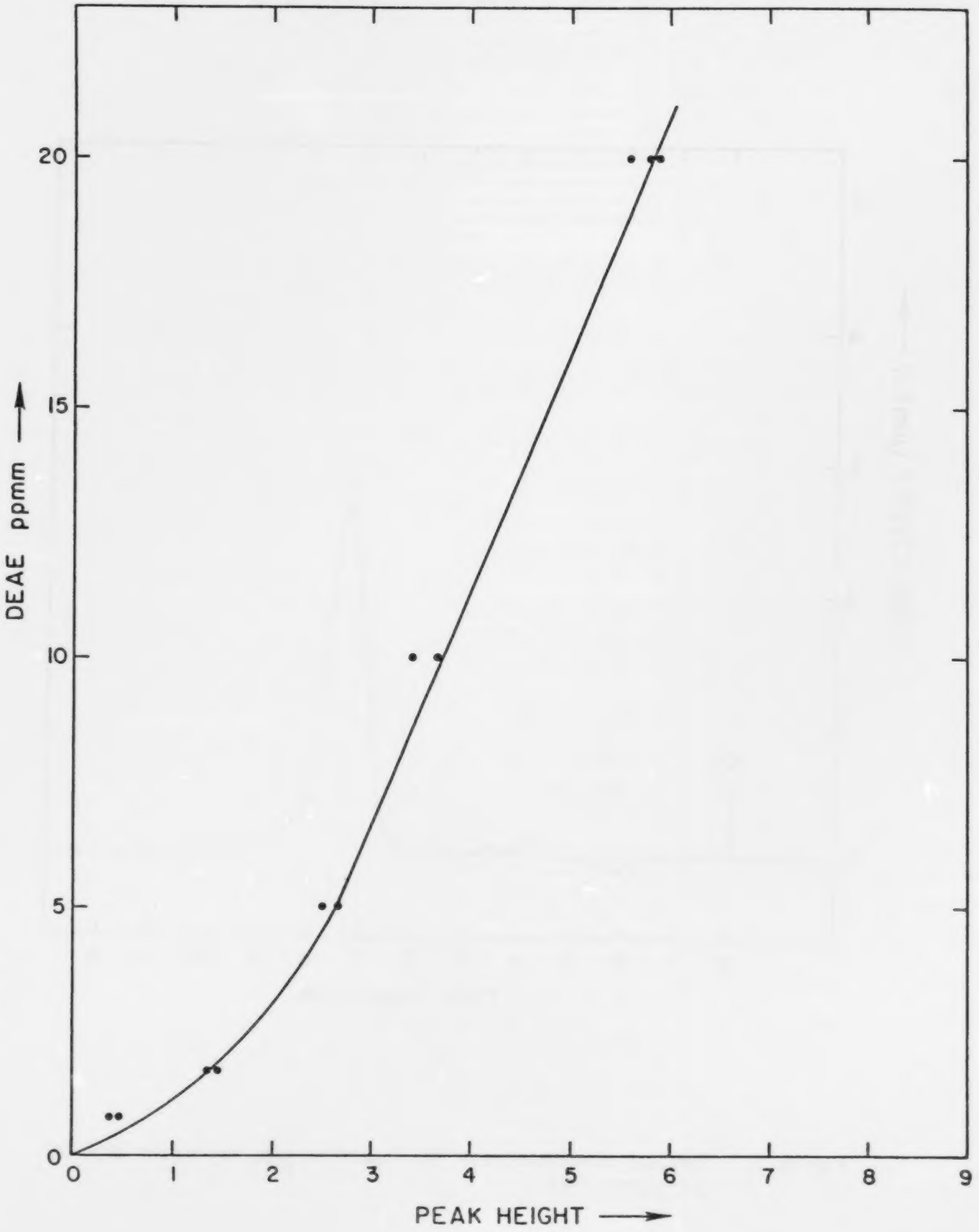


Figure 1: Calibration curve for 2-diethylaminoethanol.

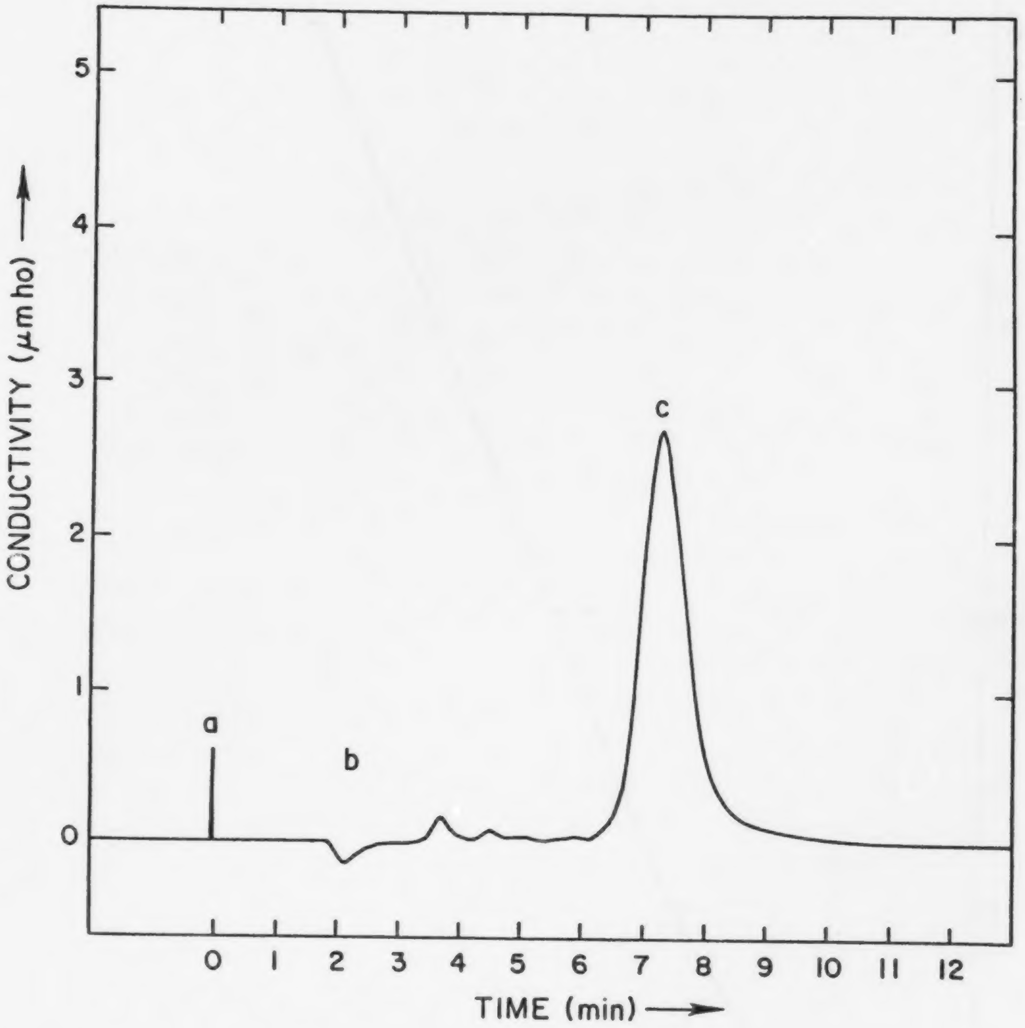


Figure 2: Typical chromatogram: (a) injection pip, (b) water dip, (c) 5.0 ppmm DEAE.

ANALYSIS OF SEMI-VOLATILE ORGANIC COMPOUNDS USING SUPERCRITICAL FLUID METHODOLOGIES

Bob W. Wright, Edward K. Chess, Clement R. Yonker and Richard D. Smith
Chemical Methods and Kinetics Section, Pacific Northwest Laboratory
(Operated by Battelle Memorial Institute) Richland, WA 99352

INTRODUCTION

Supercritical fluids possess favorable physical-chemical properties which render them useful for many analytical applications. Recently, a number of potentially important supercritical fluid based analytical methodologies have emerged which include capillary-column supercritical fluid chromatography (SFC) (1), capillary-column supercritical fluid chromatography-mass spectrometry (SFC-MS) (2), direct supercritical fluid injection-mass spectrometry (DFI-MS) (3), and direct supercritical fluid extraction-mass spectrometry (SFE-MS) (4). Although these techniques are in an early stage of development, they have shown considerable promise for the characterization of complex organic mixtures.

The compressibility of supercritical fluids is large above the critical temperature and small changes in pressure result in large changes in the density of a fluid (5). Molecular interactions increase due to shorter intermolecular distances and solvating characteristics approaching that of a liquid are imparted. However, the viscosity and the solute diffusivity remain similar to that of a gas. These properties form the basis of supercritical fluid chromatography (SFC) and result in the potential for the separation of less volatile compounds than is possible by gas chromatography and for significantly enhanced chromatographic efficiency per unit time relative to liquid chromatography. These same properties are also advantageous for the efficient removal and transport of selected organic compounds from matrix components using supercritical fluid extraction (SFE).

This study demonstrates the applicability of SFC and analytical SFE for the analysis of semi-volatile compounds. Mixtures of nitro-polycyclic aromatic hydrocarbons that are not ammenable to gas chromatography were separated using SFC with tentative compound identifications made by SFC-MS. Comparisons of analytical SFE of XAD-2 resin and NBS Urban Dust (SRM 1649) to conventional Soxhlet extraction are also discussed.

SUPERCRITICAL FLUID CHROMATOGRAPHY

The instrumentation used for capillary supercritical fluid chromatography has been previously described (6). Briefly, the apparatus used a modified syringe pump (Varian 8500) under microcomputer control to generate the high-pressure and pulse-free supply of mobile phase and a modified gas chromatograph (Hewlett-Packard 5710) to provide constant temperature conditions and flame ionization detection. A 60 nl HPLC valve (Valco C14W) and an injection splitter were used for sample introduction onto a deactivated 15m x 50 μm fused silica capillary column coated with crosslinked 5% phenyl polymethylphenylsiloxane stationary phase (7).

A capillary supercritical fluid chromatogram of a nitrated phenanthrene mixture is shown in Figure 1. Carbon dioxide at 100°C was used for the mobile phase. The pressure was programmed in such a way to create linear density ramps as indicated in the time and density legends. All five of the mononitrophenanthrene isomers were discernible and would have been completely resolved if their concentrations were lower. The mononitrophenanthrene dimers were also eluted with several isomers being separated. These dimers are not sufficiently volatile to be eluted under normal gas chromatographic conditions. A mass spectrum obtained by SFC-MS of one of these dimer isomers is shown in Figure 2. Ammonia was used for the chemical ionization reagent gas and consistent fragmentation was obtained. A similarly obtained chromatogram of a nitrated 9-hydroxyfluorene mixture is shown in Figure 3. During nitration fluorenone was also formed. Most notable, however, is the elution of the 9-hydroxynitrofluorene isomers which are thermally labile and reported to be non-gas chromatographable (8). These examples illustrate the applicability of SFC and SFC-MS for the analysis of nonvolatile and thermally labile materials.

SUPERCRITICAL FLUID EXTRACTION

Off-line analytical supercritical fluid extraction was accomplished using a small, flow-through high-pressure extraction cell. The high-pressure supply was generated using either a syringe pump (Varian 8500) or a reciprocating HPLC pump (Rainin, Rabbit HPX) that were modified to operate under pressure control. The extraction cell was maintained at constant temperature in a gas chromatographic oven. The supercritical fluid effluent was decompressed using a short length of heated 50 μm stainless steel tubing that was crimped at the exit end.

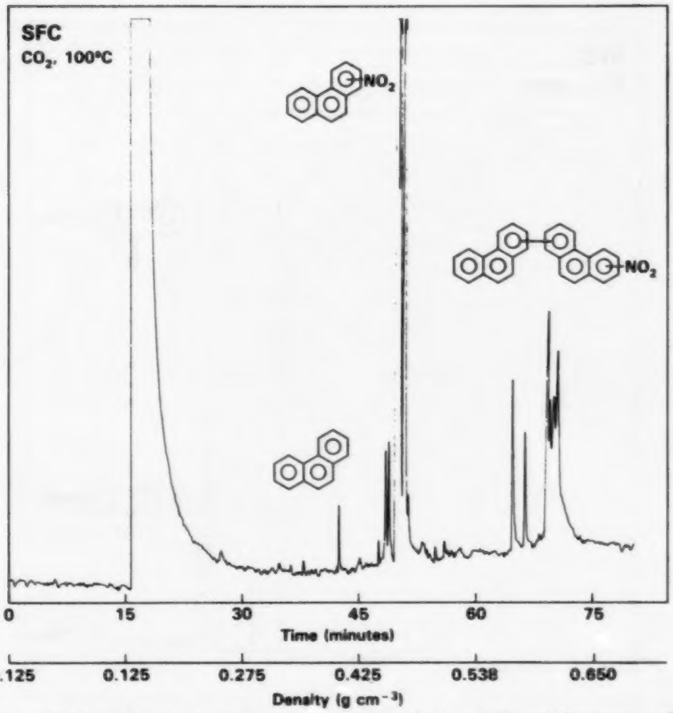


Figure 1. SFC chromatogram of nitrated phenanthrene mixture.

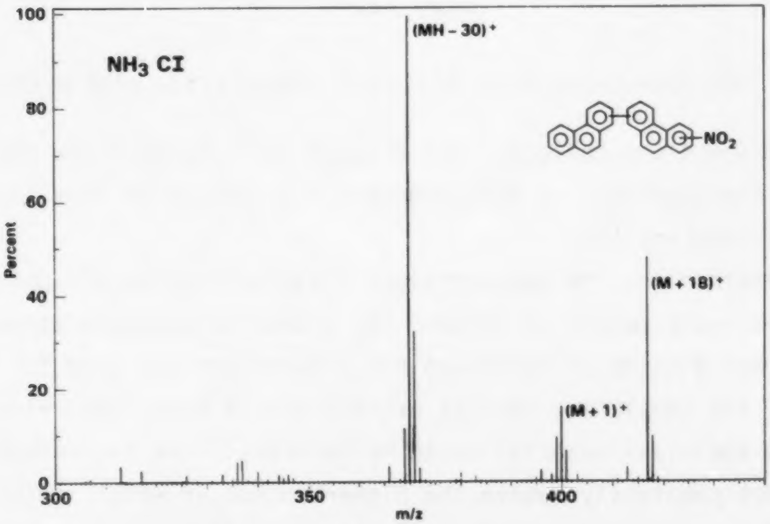


Figure 2. NH_3 CI mass spectrum of a nitrophenanthrene dimer obtained by SFC-MS.

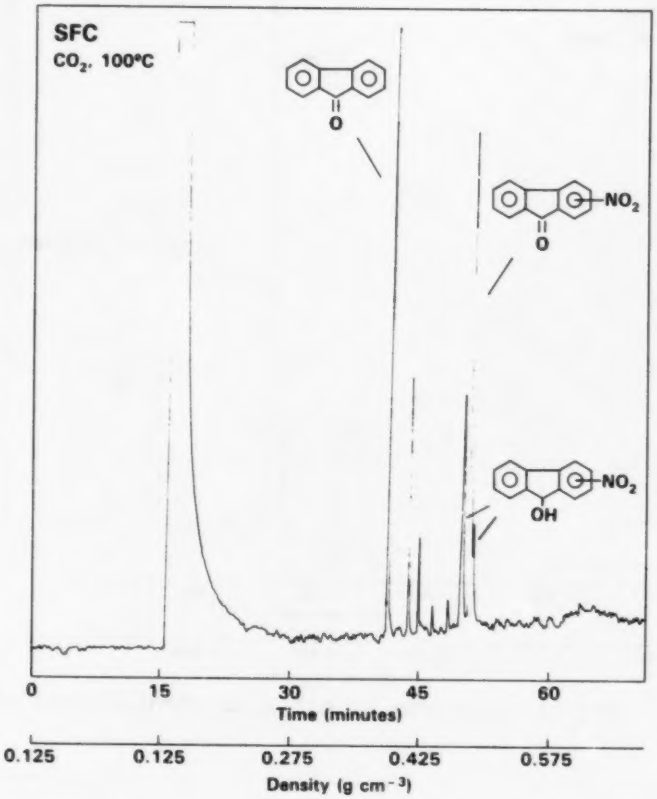


Figure 3. SFC chromatogram of nitrated 9-hydroxyfluorene mixture.

The resulting effluent was collected and trapped in a closed flask cooled to liquid nitrogen temperatures. A more complete description of this instrumentation is given elsewhere (9).

The data obtained for the supercritical fluid extraction of approximately one gram of XAD-2 resin spiked at 50 ppm with a model compound mixture is listed in Table 1. Carbon dioxide at 150°C and 400 atmospheres was used for the extraction. After SFE the sample was Soxhlet extracted with methylene chloride to determine if any additinal material could be recovered. As indicated, SFE with this fluid did not completely remove the higher molecular weight material. However, since only a small volume (∽ 200 cm^3) of extraction fluid was utilized and the larger components have lower solubility, it is reasonable that a more exhaustive extraction or modified fluid phase would have recovered the remaining material. Similar extraction data for NBS Urban Dust are compared in Table 2.

Two samples were extracted; Soxhlet extraction followed by SFE and SFE followed by Soxhlet extraction. The SFE recovered additional material not extracted by the Soxhlet extraction and only a small amount of material was recovered by Soxhlet extraction following SFE. An important point is the supercritical fluid extractions required less than a hour as compared to sixteen hours for the Soxhlet extractions. These data illustrate the potential for very rapid and efficient extractions of adsorbents and particulates to be accomplished by SFE. Even more efficient extractions can be anticipated using supercritical fluid systems with higher solvating properties.

Table 1. XAD-2 Resin Extraction Recovery

Compound	SFE[a] %	Soxhlet[b] After SFE %
Chrysene	75	0
Benzanthrone	79	1
1-Nitropyrene	83	0
Dibenzo(a,i)carbazole	95	0
Coronene	81	17
Rubrene	25	19

[a] CO_2 at 150°C and 400 atm
[b] $MeCl_2$ for 16 hrs.

Table 2. Extraction Comparison of NBS Urban Dust

	Recovery (µg/g)			
Compound	SFE[a] After Soxhlet[b]	Soxhlet[b]	SFE[a]	Soxhlet[b] After SFE[a]
Pyrene	1.9	2.6	5.9	1.3
Benzo(e)pyrene	---	0.7	1.3	---

[a] CO_2 at 125°C and 400 atm
[b] Methylene chloride at 16 hrs.

ACKNOWLEDGEMENT

This work was supported by the U.S. Department of Energy, Office of Health and Environmental Research and by the U.S. Environmental Protection Agency through a Related Services agreement with the U.S. Department of Energy under Contract DE-AC06-76RLO-1830. Although the information in this document has been funded in part by the U.S. Environmental Protection Agency under Interagency Agreement Number DW 89930650-01-1 with the U.S. Department of Energy, it does not necessarily reflect the views of the agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

REFERENCES

1. Fjeldsted, J. C. and M. L. Lee. 1984. Capillary Supercritical Fluid Chromatography. Anal. Chem. 56: 619A-628A.

2. Smith, R. D., W. D. Felix, J. C. Fjeldsted and M. L. Lee. 1982. Capillary Column Supercritical Fluid Chromatography/Mass Spectrometry. Anal. Chem. 54: 1883-1885.

3. Smith, R. D. and H. R. Udseth. 1983. Mass Spectrometry with Direct Supercritical Fluid Injection. Anal. Chem. 53: 2266-2272.

4. Smith, R. D. and H. R. Udseth. 1983. New Method for the Direct Analysis of Supercritical Fluid Coal Extraction and Liquefaction. Fuel 62: 466-468.

5. Gouw, T. H. and R. E. Jentoft. 1975. Practical Aspects in Supercritical Fluid Chromatography. Advan. Chromatogr. 13:1-40.

6. Wright, B. W. and R. D. Smith. 1984. Application of Capillary Supercritical Fluid Chromatography to the Analysis of a Middle Distillate Fuel. Chromatographia 18: 542-545.

7. Wright, B. W.,P. A. Peaden, M. L. Lee and T. J. Stark. 1982. Free-Radical Crosslinking in the Preparation of Non-Extractable Stationary Phases for Capillary Gas Chromatography. J. Chromatogr. 248: 17-34.

8. Paputa-Peck, M. C., R. S. Marano, D. Schuetzle, T. L. Riley, C. V. Hampton, T. J. Prater, L. M. Skewes, T. E. Jensen, P. H. Ruehle, L. C. Bosch and W. A. Duncan. 1983. Determination of Nitrated Polynuclear Aromatic Hydrocarbons in Particulate Extracts by Capillary Column Gas Chromatography with Nitrogen Selective Detection. Anal. Chem. 55: 1946-1954.

9. Wright, B. W. and R. D. Smith. 1985. Analytical Supercritical Fluid Extraction of Adsorbent Materials. Submitted for publication.

VALIDATION OF AN EMISSION MEASUREMENT METHOD FOR INORGANIC ARSENIC

Thomas E. Ward

Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

R. K. M. Jayanty

Research Triangle Institute
Research Triangle Park, NC 27709

ABSTRACT

The U.S. Environmental Protection Agency's Proposed Method 108 for measurement of inorganic arsenic emissions from stationary sources has been evaluated both in the laboratory and field. Details of the evaluations are given through analysis of laboratory samples, preparation of filter and impinger audit samples for field use and stability studies, and two field tests of the method using dual and quad sampling trains at a copper smelter plant and a glass manufacturing plant. Several conclusions and recommendations have been made regarding the method.

INTRODUCTION

The Environmental Monitoring Systems Laboratory (EMSL) of the U.S. Environmental Protection Agency has determined the industries and processes of stationary sources which emit significant inorganic arsenic emissions. Included among these are the five most significant sources chosen by EPA's Office of Air Quality Planning and Standards (OAQPS) for original consideration for regulation of inorganic arsenic emissions: glass plants, secondary lead smelters; primary copper smelters; cotton ginning activities; and zinc oxide manufacturing. Presently, OAQPS is recommending only primary copper smelters and glass plants for these regulations.

A primary concern of EMSL has been validation of the procedure used for sampling and analysis of the arsenic-containing emissions. EMSL determined that the proposed EPA Method 108[1], which involves collection in impinger solutions and on filters and measurement using atomic absorption spectrophotometry, was the best available method for measuring these arsenic emissions. Therefore, a program to validate this method was designed by EMSL. The validation approach included a multicomponent project which involved both laboratory and field studies. Research Triangle Institute reviewed reports describing sampling and analysis of arsenic, evaluated EPA Method 108 through analysis of laboratory samples, prepared audit samples for field use and studied the stability of audit samples. PEDCo Environmentalists, Inc., collected samples at a copper smelter and a glass manufacturing plant and analyzed the collected samples.

DISCUSSION

Laboratory studies conducted to evaluate the performance of EPA Method 108 included: recovery and measurement of audit materials, stability of audit materials, precision of the method from sample preparation to measurement, and recommendations regarding analytical aspects of the method. Standard samples containing arsenic with loadings approximating emissions expected at field test sites were prepared in the laboratory. A total of 36 impinger samples and 36 filter samples were prepared from a concentration matrix of six different impinger and filter loadings. Loadings ranged from 0.013 mg to 5.0 mg arsenic for the impinger samples and from 1.4 mg to 52 mg arsenic for the filter samples. Ampules were used to contain the impinger samples. Selected filter and impinger samples from each concentration set were analyzed by atomic absorption spectrophotometry. The precision of the analytical phase of Method 108 was determined from triplicate analyses of standards. The relative standard deviation (RSD) of the analytical method was approximately 1.0 percent in the 40- to 100-micrograms arsenic per milliliter (μg As/ml) high concentration range; and in the low concentration analysis range, approximately 1.0% at the 0.15 μg As/ml level, and 7% near the detection limit level of 0.01 μg As/ml. The stability of both simulated sample types (impinger and filter) for potential use as audit materials for EPA Proposed Method 108 was also evaluated over a six-month period. Stability as a function of sample type, concentration level and time was evaluated. Changes in concentration level and time were evaluated. Changes in concentration were calculated to average -0.04% per day, which is sufficient to prescribe an acceptable period of usefulness for the samples as audit material.

Two field tests to validate proposed Method 108 at different sites were conducted. The first field test was conducted at a primary copper smelter (Plant No. 1) and the second test was conducted at a glass manufacturing facility (Plant No. 2). During the field test series, PEDCo conducted a total of 14 tests of proposed Method 108 (seven paired[2] runs) at Plant No. 1 and a total of 36 tests of proposed Method 108 (nine quad-train[2] runs) at Plant No. 2 to determine the precision of the methodology for measuring arsenic concentrations. A comparison of the statistical results for total arsenic from Plant No. 1 indicates that the within-run RSD for the seven sample runs ranged between 3.9 and 22.8 percent with the value for precision of the method at 15.7 percent. Standard deviations of paired runs had a low value of 0.36 mg/dNm^3, a high of 4.06 mg/dNm^3, and a pooled mean of 1.90 mg/dNm^3. The mean arsenic concentration of paired runs ranged from 3.08 to 18.3 mg/dNm^3 based on total arsenic, and the overall mean value was 10.5 mg/dNm^3. Considering the sampling site constraints and variable process operation, the results indicate that an acceptable degree of precision was achieved at this source.

The standard deviations of the quad run (Plant No. 2) had a low value of 0.10 mg/dNm^3, a high value of 0.51 mg/dNm^3, and a pooled mean value of 0.37 mg/dNm^3. The RSD values ranged from 0.95 to 5.5 percent, with the value for the precision of the method at RSD value of 3.85 percent. The mean arsenic concentration of the individual quad runs ranged from 9.18 to 10.55 mg/dNm^3 with an overall mean of 9.67 mg/dNm^3, which indicated a generally consistent process operation throughout the test period. Once again, the results indicated that an acceptable degree of precision was achieved. The detailed results of all tests are presented in the project report[3].

CONCLUSIONS AND RECOMMENDATIONS

Several conclusions and recommendaitons have been made regarding the proposed EPA Method 108 for the determination of arsenic emissions from stationary sources. These include: (1) the method is relatively straightforward and is reasonable with respect to time and cost; (2) during its preparation, greater care of the sample should be exercised than the proposed method requires, including avoidance of bumping and spattering during the evaporation process; (3) filter and impinger audit samples were found to have an acceptable period of usefulness based upon a six-month stability study; and (4) an acceptable degree of precision of Method 108 is achieved from the field tests. Graphite furnace atomic absorption techniques have an improved analytical range over hydride techniques, are more rapid and, therefore, are recommended to be an adequate measurement substitute.

REFERENCES

1. Federal Register, "EPA Proposed Method 108 - Determination of Particulate and Gaseous Arsenic Emissions," Vol. 48, No. 140: pp 33166-33172.

2. Mitchell, W. J., and M. R. Midgett. "A Means to Evaluate the Performance of Stationary source Test Methods," Env. Sci. Tech. 10: 85-88 (1976).
3. Ward, T. E., et al. Validation of an Emission Measurement Method for Inorganic Arsenic from Stationary Sources: Proposed Method 108 - Laboratory and Field Test Evaluations. EPA-600/4-84-080, October 1984.

STUDIES ON THE DYNAMIC IMPINGER SAMPLING SYSTEM

J. C. Pau, J. E. Knoll and M. R. Midgett

The dynamic impinger sampling system uses a fixed-bed, counter-current impinger to collect gaseous samples into an absorbing solvent. The flow rates of both the liquid solvent and the gaseous sample are controlled by use of peristaltic pumps. The temperature of the absorbing solvent is controlled by use of a constant-temperature bath. The dual dynamic impinger sampling system uses two impingers in parallel and two multi-channel peristaltic pumps to control the liquid and gas sample flow rates. In the dual dynamic impinger sampling system, duplicate samples are taken, and the precision of the sample collection can be measured directly.

Many improvements in the design of the dynamic impinger sampling system were made last year. The impinger size was changed, and the impinger liquid level control was added. Different packing materials were studied for their sampling efficiencies. Teflon turnings which were 1/8" wide and 4/1000" thick were better than either glass beads or silica chips.

The dynamic impinger sampling system was modified for the long-term operational stability which was needed in the field test. An additional peristaltic pump was used to control the liquid levels in the impingers. A check valve and a carbon absorber were put in between the impinger and the gas sample pump to reduce the ripples in the gas sample flow rate and to prevent the solvent vapors from reaching the pump tubing on the gas sample pump.

A peristaltic pump would not control the flow rates between the two channels better than 1 to 2%, and in long-term operations this difference in the flow rates could cause either the liquid level to drop significantly, or to overflow the system. A second pump had to be added to this system to control the liquid levels inside the impingers. The gas sample flow rate change was caused by the changes in the liquid levels inside the impingers that changed the pressure drop across the system, and the erosion of the gum rubber pump tubing on the gas sample pump by the solvent vapors which changed the pumping efficiency of the tubing. A check valve and a carbon absorber were added between the impinger and the gas sample pump. This reduced the ripples in the gas flow rate and prevented the solvent vapors from reaching the gum rubber tubing.

Two field tests were conducted last year; the first one at a vinyl chloride manomer plant for vinyl chloride, and the second one at a degreasing plant for methylchloroform. The vinyl chloride was collected by a dual dynamic impinger sampling system with the impinger and the absorbing solvent (iso-octane) set at -20°C. The gas flow rate was set at 7.5 ml/min, and the liquid flow rate was at 1 ml/min. The sample solutions were sealed in serum bottles and brought back to the laboratory for analyses. A gas chromatograph equipped with an electron capture detector was used for the analyses. The analytical results were compared to EPA reference Method 106 and the continuous emission monitor installed at the test site under another EPA evaluation program. The analytical results revealed that the precision of the dual impingers was about 15%, and the relative accuracy of the method compared to Method 106 was about 20%. We note here that the detection limit of this system was estimated as approximately 1 ppm, and whenever the vinyl chloride level dropped to below 2 ppm, the precision and accuracy values became very poor. The major problem for the vinyl chloride sample collection was the control of the sampling temperature at below -20°C throughout the sampling time.

The sampling of the methylchloroform at a degreasing plant was relatively simple. The EPA reference Method 23 Tedlar bag sampling technique was used to collect the sample, which was analyzed the following day for comparison. Both precision and accuracy of this species was about 15%.

DEVELOPMENT OF A COMPACT TOTAL REDUCED SULFUR (TRS) CONTINUOUS EMISSION MONITORING SYSTEM

Herbert R. Defriez, TRS Systems, Inc.
John W. Short, Harmon Engineering & Testing
Terence A. Whitt, Harmon Engineering & Testing

For the past several years EPA regulations have required that the kraft pulp industry install continuous emission monitors (CEMs) at all new or newly-modified sources of total reduced sulfur (TRS). The regulations will soon be expanded to include all older TRS sources as well, greatly expanding the need for TRS CEMs. The TRS 2000 is an instrument of innovative design that provides reliable continuous monitoring of TRS emissions in a compact stack-mountable package.

The TRS 2000 is a single on-stack unit small enough to be carried by two men. Since all sampling and analytical systems are on the stack, sample lines are very short. A moderate flow rate is used along with in-stack sample dilution which results in a very low net sampling rate and minimal loading of filters and scrubbers. The low sampling rate and an aerodynamically designed probe tip reduce particulate loading to such low levels that backflushes will be infrequent and short, and filter replacement will be reduced to quarterly or longer intervals. One of the design objectives is to reduce all maintenance to such intervals so that all maintenance and repairs may be done in infrequent visits by factory representatives with no need for mill personnel to be involved.

The TRS 2000 uses a rapidly-reporting analytical system which, along with the short sample lines and low overall system volume, provides nearly instantaneous response to changes in the source concentration. The low sampling rate allows for the use of a self-contained permeation-type calibration system. Permeation devices provide NBS traceable calibration standards, are stable for months, and are inexpensively replaced. All systems in the TRS 2000 are operated automatically by an on-board computer. Data are transmitted to a remote data terminal by FM radio, eliminating the need for data cables.

Sample dilution is accomplished by the loop-dilution concept developed by Defriez. Instead of requiring a separate source of dilution gas, a portion of the sample flow leaving the analyzer is returned to the probe as dilution air, see Figure 1. The total intake flow at the probe is greater than the dilution flow and the difference is made up by stack gases entering the probe tip. The valves and orifice governing the flow rates are enclosed in a heated chamber for stability. These are downstream from all analytical equipment, including the dryer. It can be seen that for a dry sample such as calibration gas the total intake flow and the orifice flow are equal and that the net sample intake flow equals the dump flow. When the system is changed to wet stack gas, the orifice, dump and dilution flows do not change; the gas flowing through the controlling orifice and valves remains dry. However, the removal of moisture by the dryer increases the total intake flow, thus increasing the net sample intake flow and reducing the dilution ratio. This action causes an automatic adjustment of the analyzer response so that all valves are given in the dry-gas basis of the calibration gas. Because of the low total system volume, response to changes in stack moisture is rapid. The TRS 2000 uses an orifice flow of about 1/2 L/min and a dilution ration of about 20-25 to 1.

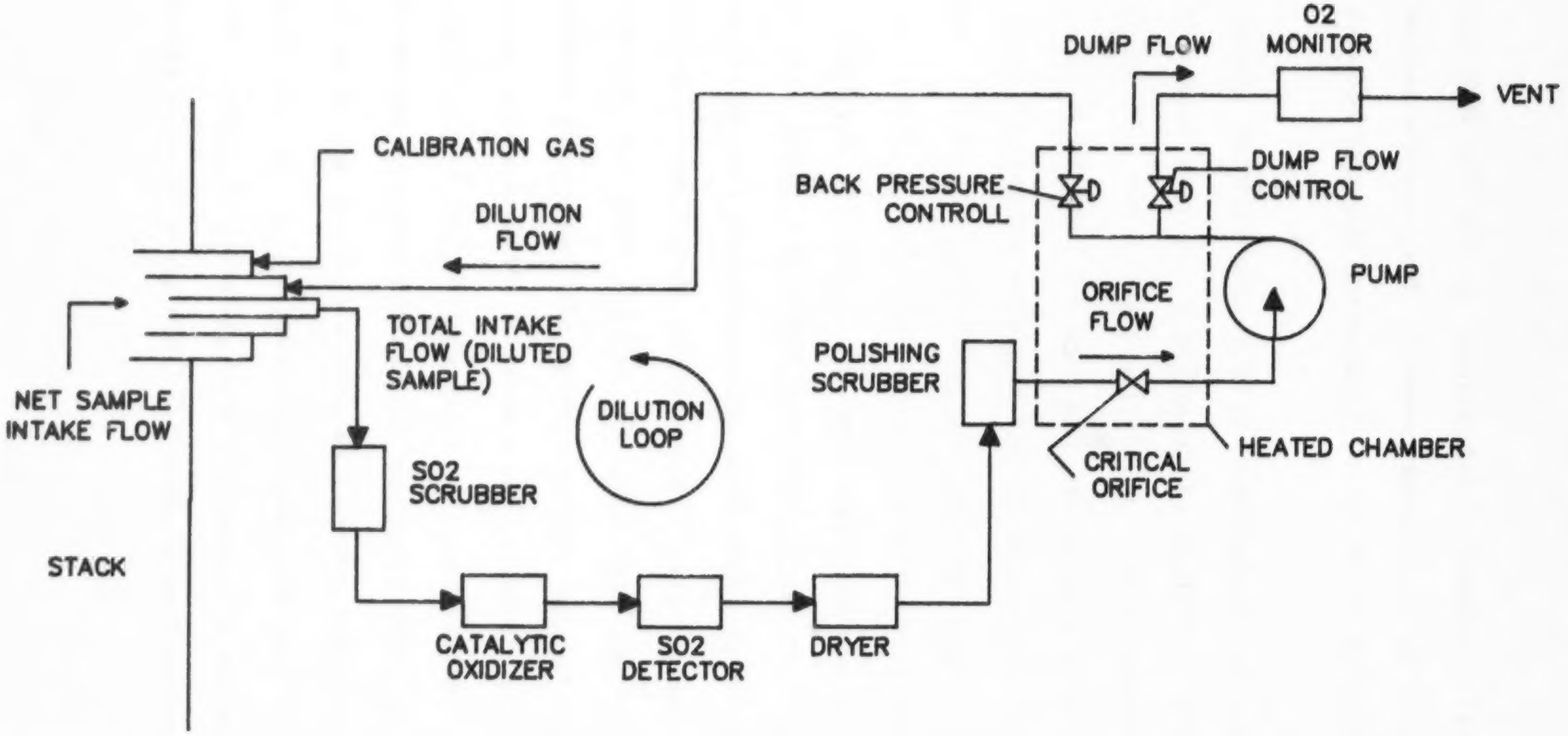

CALIBRATION GAS
DILUTION FLOW
NET SAMPLE INTAKE FLOW
TOTAL INTAKE FLOW (DILUTED SAMPLE)
STACK
SO2 SCRUBBER
DILUTION LOOP
CATALYTIC OXIDIZER
SO2 DETECTOR
DRYER
POLISHING SCRUBBER
BACK PRESSURE CONTROLL
DUMP FLOW
O2 MONITOR
VENT
DUMP FLOW CONTROL
PUMP
ORIFICE FLOW
CRITICAL ORIFICE
HEATED CHAMBER

FIGURE 1
ANALYTICAL SYSTEM AND LOOP
IN THE TRS 2000

The analyzer system operates by removal of existing sulfur dioxide, oxidation of TRS to SO_2, and measurement of the produced SO_2. Oxidation is effected by a catalytic device which offers several advantages over traditional quartz tube-furnace oxidizers: rugged all-metal construction, lower operating temperature (325°C rather than 800°C), carbonyl sulfide (COS) not converted. Laboratory and field tests have shown the catalytic oxidizer to be efficient and accurate in the analysis of the four TRS compounds controlled in standards of performance for kraft pulp mills. The SO_2 analyzer is a Monitor Labs pulsed-fluorescence detector of proven accuracy, ruggedness and dependability.

Calibration gases are introduced at the probe tip, thus calibrating the entire system. The dryer is a permeation type and is followed by a polishing scrubber that contains activated charcoal to remove unoxidized organics that could otherwise build up in the loop and possibly cause interferences. A fuel-cell type oxygen monitor is placed in the dilution dump outlet.

Probes are custom made to suit conditions in the stacks to be monitored. The probe sheath is Hastaloy and interval parts are Hastaloy or Teflon. Sample lines and system tubing are of Teflon or stainless steel. Leak-free rotary valves are used for such functions as backflush and calibration. Built-in safeguards prevent damage from occurrences as intrusion of liquid coater or loss of control air. The efficiency of the SO_2 scrubber is automatically checked by passing the catalytic oxidizer. Data from the SO_2 and O_2 analyzers are converted to digital from by the control computer. These data are then transmitted over the FM data link with several error checking routines such as redundant transmission and check bits; this ensures that accurate data are received by the output terminal.

Field trials of the TRS 2000 have been conducted at a number of Southern pulp mills. These trials have been conducted at recovery boilers and at calcining facilities under a variety of conditions of stack temperature and moisture, particulate loading, TRS concentration, and weather. The system has proven to be reliable, and comparisons of data with Method 16 data or with data from previously installed, certified CEM's have shown that accurate results are obtained and proven that the TRS 2000 is certifiable to the standards of PS-5.

MEASURING VOLATILIZATION FLUX OF PESTICIDES FROM TREATED SURFACES

Michael Majewski, James Woodrow, James Seiber and Paul Sanders
Department of Environmental Toxicology
University of California
Davis, CA 95616

We have been looking at the entry of pesticides in the atmosphere through volatilization from agricultural surfaces. Among our objectives is comparison of volatilization rates for chemicals with wide ranges of properties using the EXAMS computer model, a laboratory chamber, field measurements and simple estimation methods.

The pesticides studied vary considerably in water solubility (S) and vapor pressure (P) and, therefore, the Henry's law constant (H = P/S) (Table 1). According to the H constant, mevinphos and ionized MCPA, with low values, would be expected to show low rates, while compounds such as diazinon and molinate with higher H values should show higher rates of volatilization from water.

TABLE 1. PHYSICAL PROPERTIES (at 22°C unless otherwise specified)

Compound	MW	Water Solubility[a]	Vapor Pressure[b]	Henry's Law Constant[c]
Mevinphos	224	miscible	2200.0	0.052
MCPA DMA	245	>300,000(25°C)	0.1(25°C)	<0.00001(25°C)
Thiobencarb	258	30(20°C)	1.5(15.3)[d](20°C)	1.7(17.0)[d](20°C)
Parathion	291	12	6.0	18.7
Diazinon	304	69	162.0	94.0
Molinate	187	800(20°C)	3110.0(25°C)	96 (20°C)

[a] mg/L [b] $\times 10^{-6}$ mmHg [c] $\times 10^{-8}$ $(m^3 \cdot atm)/mole$ [d] remeasured value

Predicting volatilization rates from moist soil requires another physical property, the soil binding constant (K_d). By using a volatilization factor (f) where $f = p/(S \cdot K_d)$, a group of compounds can be ranked with respect to their volatilization from soil (Thomas, 1982).

The EXAMS computer model can calculate compartmental distribution, rate constants for individual fate processes and system purification times for contaminated bodies of water (Burns et al., 1981). In order to perform the calculation of interest, environmental conditions along with the compound's physical and chemical properties are entered. Our choice for several of the environmental parameters were based on the dimensions and microclimate of our laboratory chamber.

The results of EXAMS for volatilization from water (given as flux with units of $ng/cm^2 \cdot hr$ and normalized by the water concentration) show the same trend for this series of compounds as the H values (Table 2). This was not an unexpected result because EXAMS uses a two film model for volatilization for which H is a primary determinant.

The experimental laboratory chamber was as described previously (Sanders and Seiber, 1983). The measured chamber flux, normalized for concentration, agreed quite well (within a factor of two or three) with the EXAMS predictions for most of the chemicals studied (Table 2). Exceptions occur with every water soluble compounds such as mevinphos. This is because the method of estimating H from S and P does not hold for strictly hydrophyllic compounds. The EXAMS and chamber value for thiobencarb also did not agree. In this case we feel that the EXAMS value was in error due to an erroneous H value. We remeasured the P and found that it was approximately 10X larger than the reported value Herbicide Handbook (1983). Using the new P value in the EXAMS model the resulting flux agreed fairly well with both the chamber and field data.

TABLE 2. FLUX FROM WATER

Compound	H[a]	EXAMS[b]	Chamber[b]	Rice Field[b]
Mevinphos	0.052	0.017	0.15	--
MCPA DMA	1.1×10^5	0.00(pH 7)	0.00(pH 7)	2.3
Thiobencarb	17.0	0.45(4.5)[c]	13.4	13.1
Parathion	18.7	4.62	12.6	--
Diazinon	94.0	22.7	28.6	--
Molinate	96.0	51.5	62.8	77.0

[a] $m^3 \cdot atm/mole$ [b] $ng/cm^2 \cdot hr \cdot ppm$ [c] using remeasured P

For field flux measurements, the aerodynamic method developed by Taylor and coworkers (1976) was used. The method requires that the concentration of the compound of interest be measured at two or more heights above the treated surface along with wind speed, direction, and temperature. In one experiment with a rice paddy, we took simultaneous high volume air samples at two heights. The sampling station was located at the downwind edge of the field on a pier which extended into the water. The air samples as well as field water samples were taken at regular intervals for several days.

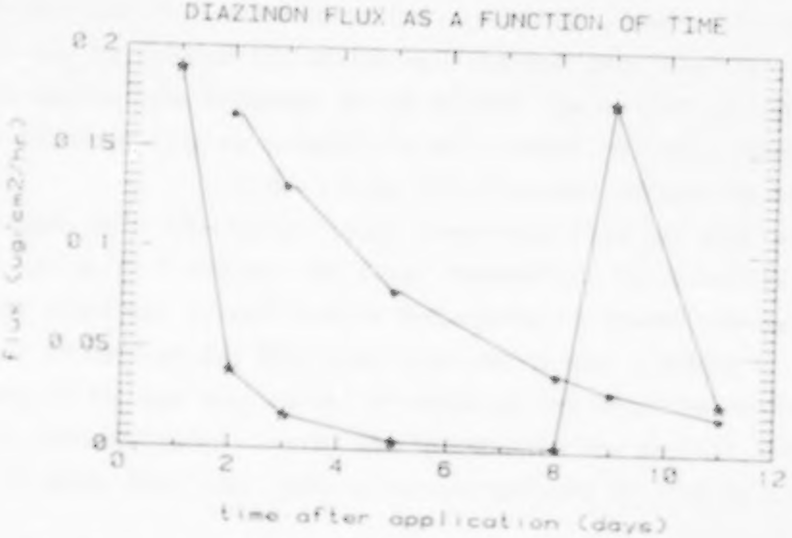
The day 1 flux data for this experiment agreed quite well with chamber and EXAMS values for molinate and thiobencarb (when the correct P value was used in EXAMS). MCPA, however, showed an unexpected higher flux in the field than predicted. This is probably due to the fact that MCPA was applied as an aqueous spray 2-3 weeks after molinate and thiobencarb (which were applied in granular form) when the rice foliage was well out of the water. Volatilization from this added surface area as well as the application method could contribute to the observed MCPA flux.

The other field experiment involved measuring pesticide flux from a fallow field. Because EXAMS does not apply to this situation, we chose to compare the measured field flux to values predicted from the Dow method. The Dow method uses the S, P and K_{oc} of a compound to determine half life in soil (Thomas, 1982). By assuming a first order process, a rate constant for volatilization can be calculated. Also, knowing the application rate and assuming the loss is due entirely to volatilization, a flux value can be estimated.

A plot of the average flux/hr as a function of time (Figure 1) shows that the intial field-measured flux (0.18 ng/cm^2·hr) was lower than predicted (0.761 ng/cm^2·hr, not shown) and that the daily flux falls off more rapidly than is predicted. There may be several explanations for these differences. The most obvious is the assumption that the entire loss is due to volatilization. If other dissipative process are occurring, measured flux must be lower than predicted. Also, the Dow method assumes that volatilization is occurring only from the surface and that no migratory processes are involved such as leaching. This method also does not take into account the effect of changing soil moisture content which occurs in the field.

Diazinon was applied in granular form and the field was then immediately irrigated. By day 4 the field surface was completely dry. On day 8, the field was again watered. Figure 1 shows that a dramatic increase in flux coincided with this second watering. This was as expected from previous studies (Spencer and Cliath, 1973).

FIGURE 1.



* = calculated flux

☆ = measured flux

In summary, the EXAMS computer model is adaptable to static water situations as occur in rice fields, giving a rapid assessment of relative volatilization rates. The EXAMS model can also be adapted to moist soil situations. The chamber was useful as a tool for determining volatilization from water and soil, yielding results in good agreement with both EXAMS and field data. Collecting field data is very expensive, labor intensive and is often of low precision. Improvements in sampling techniques and methodology are necessary before field flux measurements can be used to accurately provide data for model validation, although our preliminary results have been promising. Simple mathematical estimation methods such as the Dow equation, can determine trends in environmental behavior, but may be too oversimplified to adequately describe field conditions.

REFERENCES

1) Burns, L.A., D.M. Cline, and R.R. Lassiter, 1981, EPA report, EPA-600/3.82-023, U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

2) Herbicide Handbook of the Weed Science Society of America, 5th Edition, 1983, published by Weed Science Society of America, Champaign, IL.

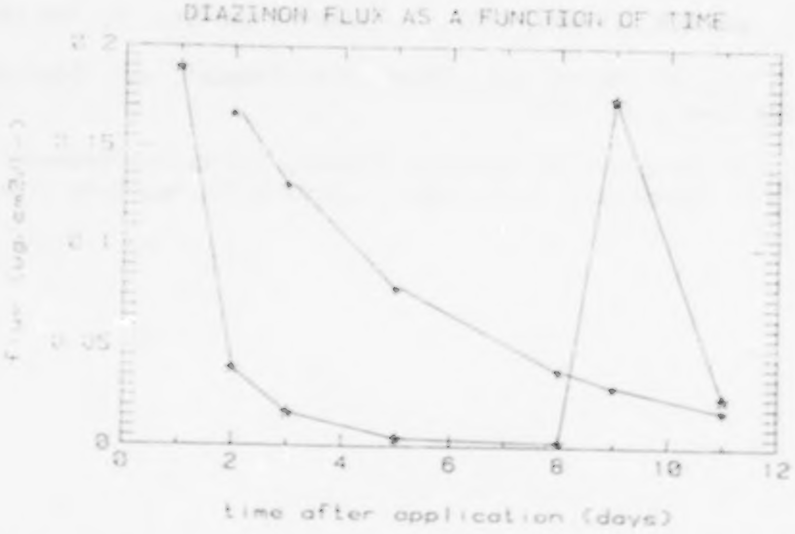
3) Sanders, P.F. and J.N. Seiber, 1983, Chemosphere, 12, 999.

4) Spencer, W.F. and M.M. Cliath, 1973, J. Environ. Quality, 2, 284-289.

5) Taylor, A.W., D.E. Glotfelty, B.L. Glass, H.P. Freeman, W.M. Edwards, 1976, J. Agric. Food Chem., 24, 625.

6) Thomas, R.G., in "Handbook of Chemical Property Estimation Methods", Lyman, W.J. Reehl, W.F. Rosenblatt, D.H., Eds., McGraw-Hill, New York, 1982, pp 16-25 to 16-27.

FIGURE 1.



* = calculated flux

☆ = measured flux

In summary, the EXAMS computer model is adaptable to static water situations as occur in rice fields, giving a rapid assessment of relative volatilization rates. The EXAMS model can also be adapted to moist soil situations. The chamber was useful as a tool for determining volatilization from water and soil, yielding results in good agreement with both EXAMS and field data. Collecting field data is very expensive, labor intensive and is often of low precision. Improvements in sampling techniques and methodology are necessary before field flux measurements can be used to accurately provide data for model validation, although our preliminary results have been promising. Simple mathematical estimation methods such as the Dow equation, can determine trends in environmental behavior, but may be too oversimplified to adequately describe field conditions.

REFERENCES

1) Burns, L.A., D.M. Cline, and R.R. Lassiter, 1981, EPA report, EPA-600/3.82-023, U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

2) Herbicide Handbook of the Weed Science Society of America, 5th Edition, 1983, published by Weed Science Society of America, Champaign, IL.

3) Sanders, P.F. and J.N. Seiber, 1983, Chemosphere, 12, 999.

☆U.S. GOVERNMENT PRINTING OFFICE: 1986-646-116-20743